

Interpreting EELS Fine Structure



Notes to accompany the lectures delivered by David A. Muller at the Summer School on Electron Microscopy: Fundamental Limits and New Science held at Cornell University, July 13-15, 2006.

Reading and References:

J.G. Chen / Surface Science Reports 30 (1997) 1–152 Fingerprints of most materials

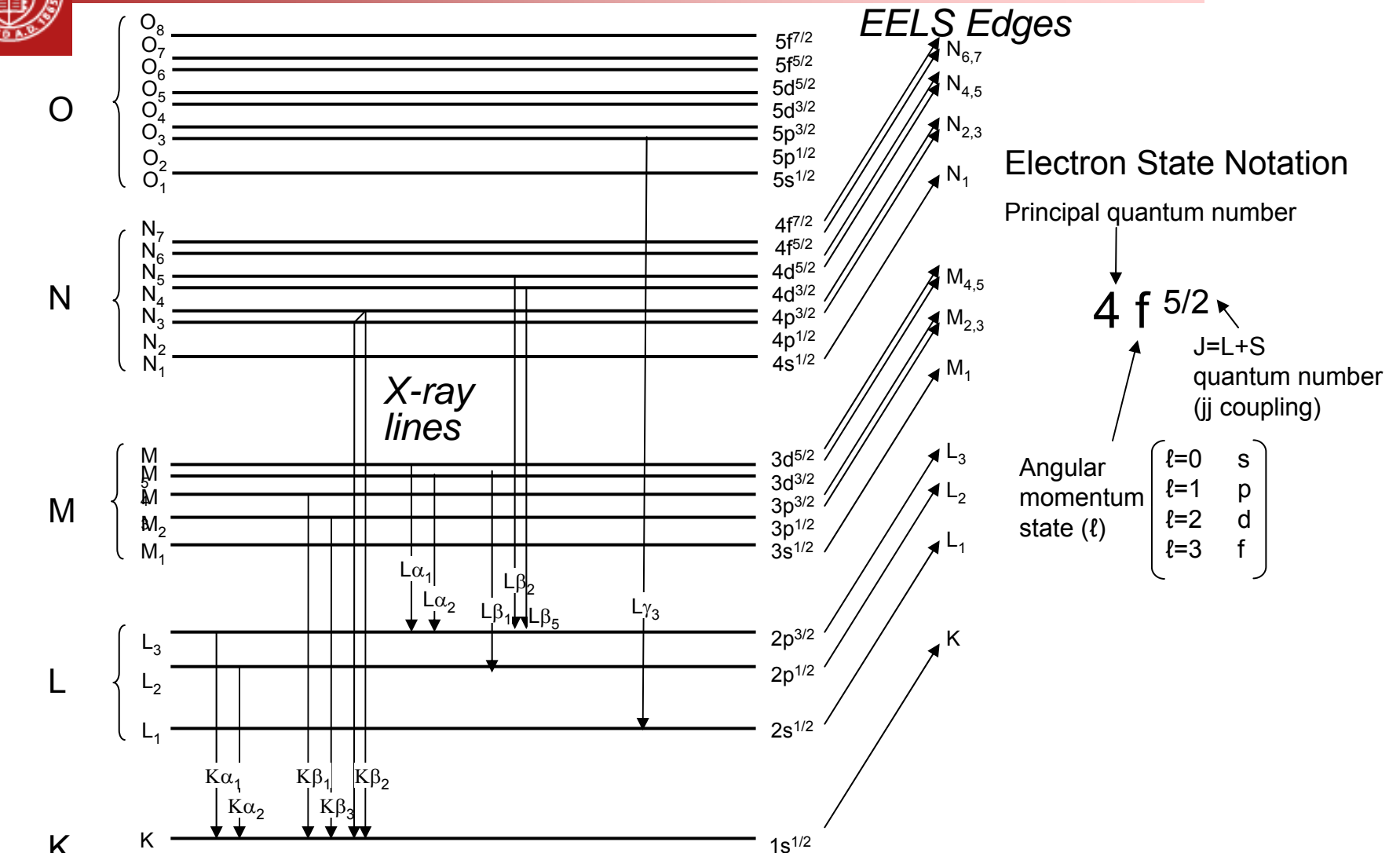
*Muller, Singh and Silcox, Phys Rev **B57**, 8181 (1998) Theory of EELS as a LDOS*

V. Keast et al, Journal of Microscopy, Vol. 203, Pt 2, August 2001, pp. 135–175.

(review of EELS)



Electron Shells and Transitions



SHELL EELS transitions are named by the initial state (e.g. $2p^{3/2} \rightarrow [3s^{1/2} 3d^{5/2}, 3d^{5/2}]$ is just L $_3$)

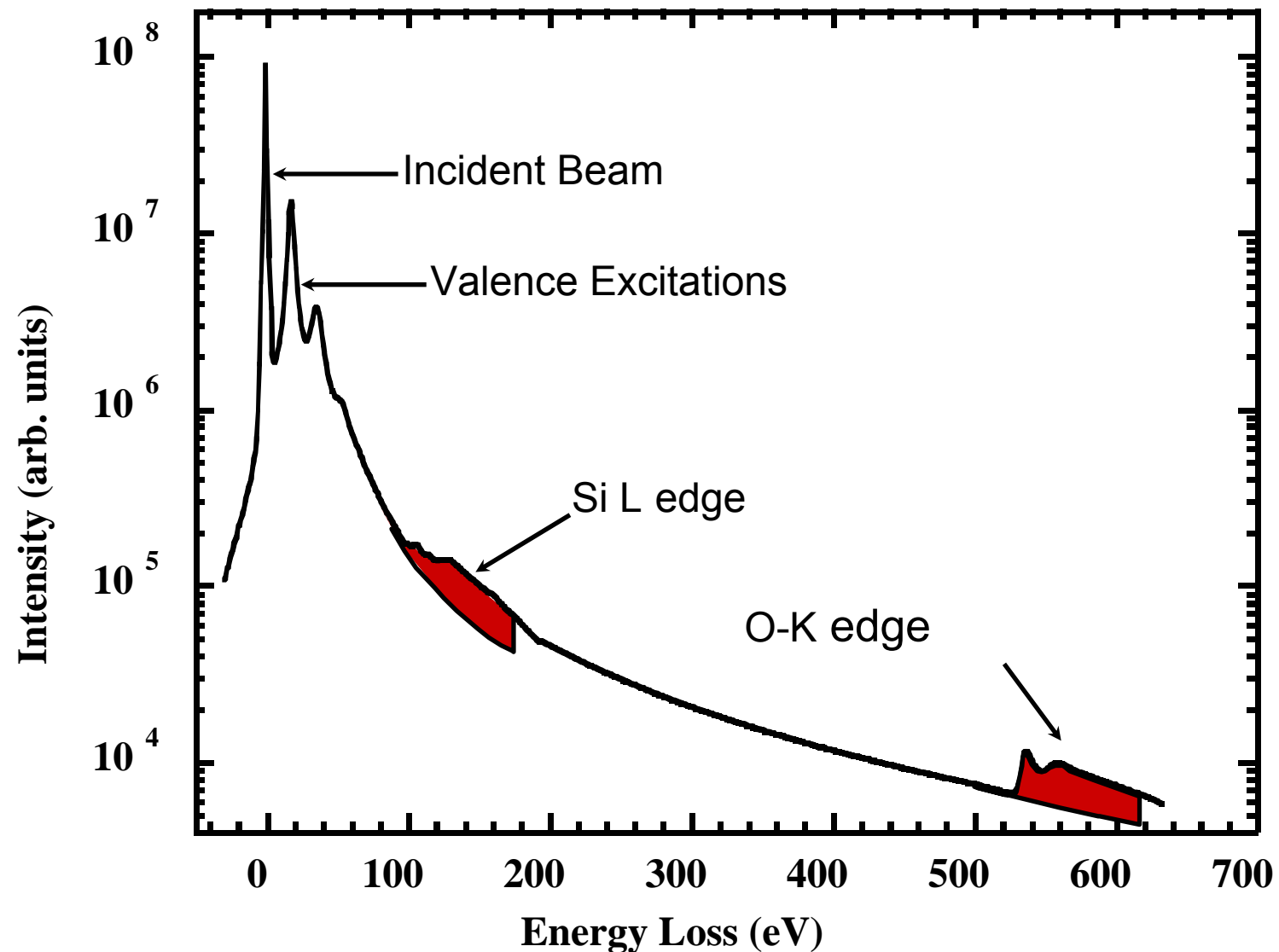
EDX transitions are named by the initial core-hole state, the emission line, and the line strength (1 is the strongest,) (e.g. $3d^{5/2} \rightarrow 1s^{1/2}$ is K α_1)

AES transitions are named by initial ionization, filling shell, shell of ejected electron (e.g. KL $_2$ L $_2$)



Electron Energy Loss Spectrum of SiO_2

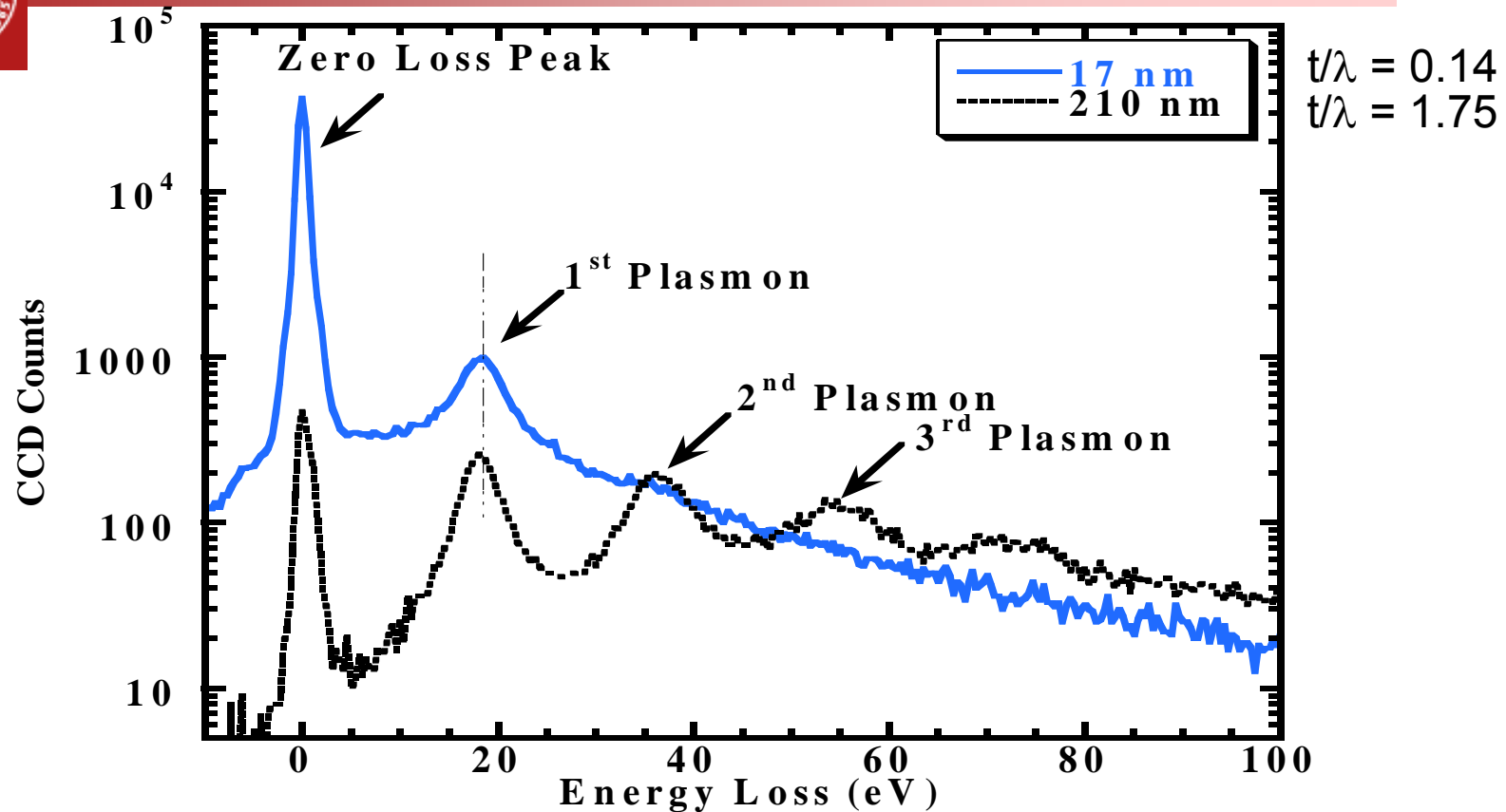
Each edge sits on the tails of the preceeding edges -> Backgrounds are large



Energy Loss Spectrum of a 100 keV Electron Beam in Si



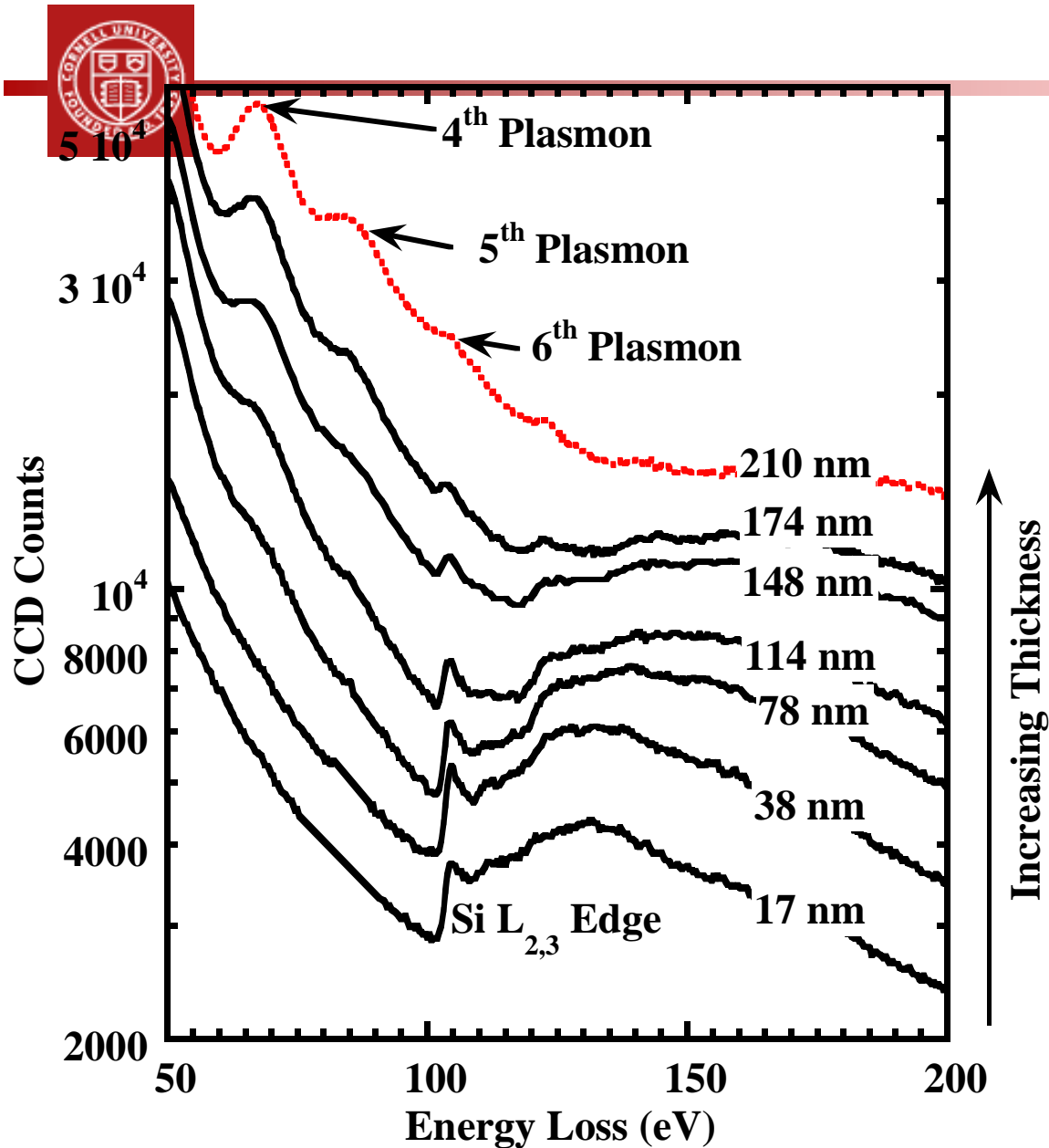
Plasmon mean free path $\lambda \sim 120$ nm



In the thinner film (17 nm thick), only single scattering has occurred, and there is a single peak at the plasma energy (~ 17 eV) – this is also called a plasmon.

In the thicker film (210 nm), a significant portion of the electron beam has undergone inelastic scattering many times. In each scattering event it loses ~ 17 eV – so those electrons that have scattered twice show up as a peak at $2 \times 17 = 34$ eV, those that scattered 3 times at $3 \times 17 = 51$ eV and so on.

Effect of Thickness on the Si L_{23} Edge at 100 kV



- Plasmon Mean Free Path in Silicon $\lambda_p \approx 120$ nm.
- When the thickness $t/\lambda_p > 1$ multiple plasmon scattering dominates the EELS spectra.
- At 210 nm, a ratio map at the 100 eV will measure the 6th plasmon, not the Si L edge!

Moral: EELS needs thin samples!

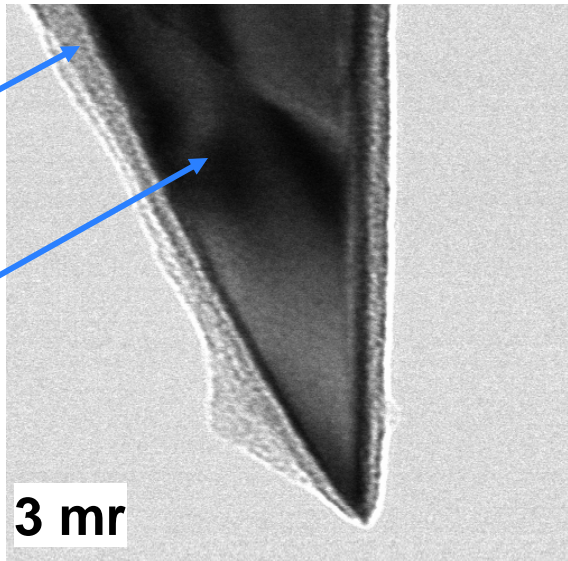
Effect of Increasing the Illumination Angle (α)

(by reciprocity: increasing the collector angle in STEM)



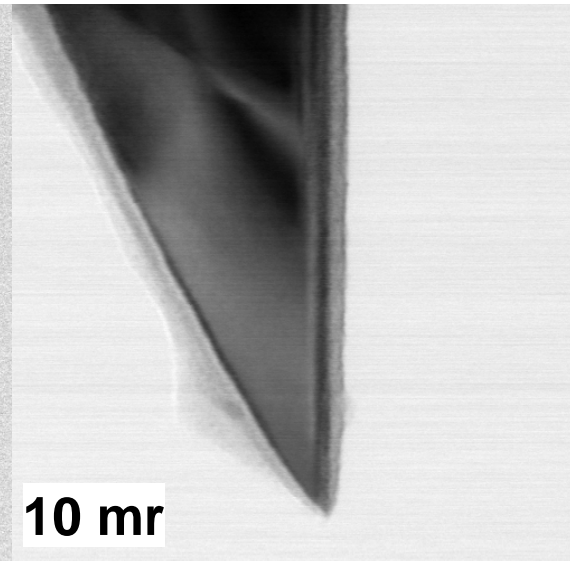
$$\alpha \ll \theta_{obj}$$

- Phase contrast
- Diffraction contrast



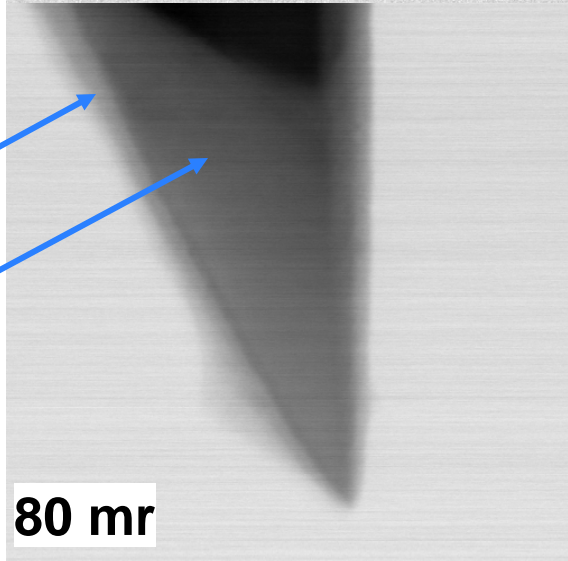
$$\alpha \approx \theta_{obj}$$

- No Phase contrast
- Diffraction contrast

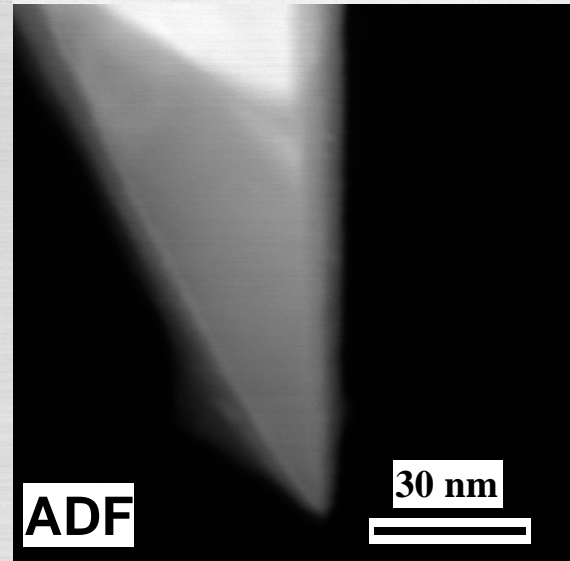


$$\alpha \gg \theta_{obj}$$

- No Phase contrast
- No Diffraction contrast



The incoherent BF image is the complement of the ADF image

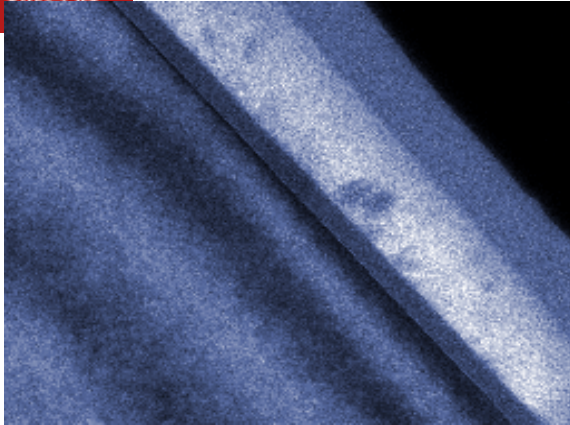


Effect of Increasing the Illumination Angle

(by reciprocity: increasing the collector angle in STEM)

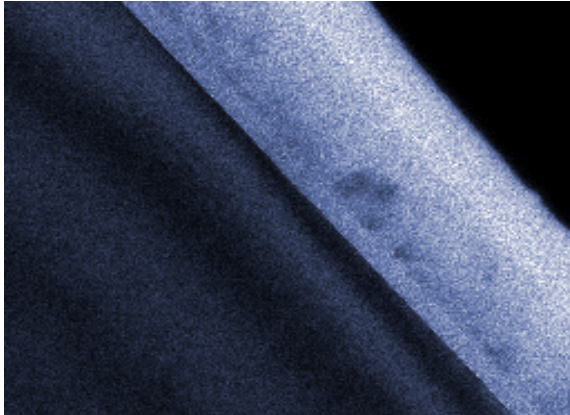
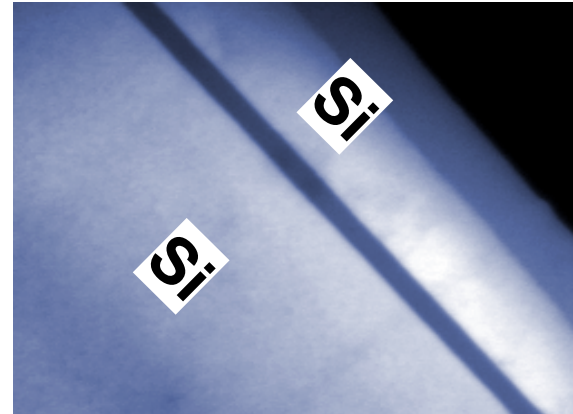


1.5 mr

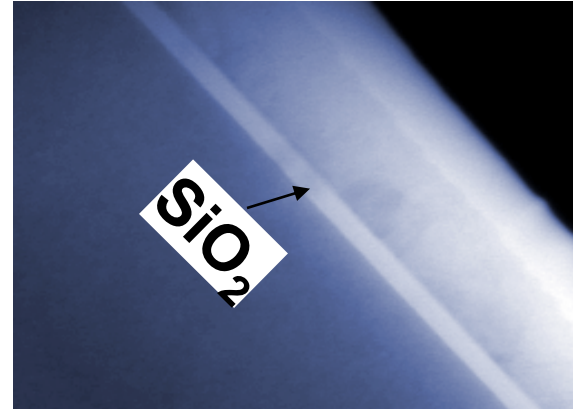


17 eV
(Si Plasmon)

80 mr



23 eV
(SiO₂ Plasmon)



Coherent Illumination:

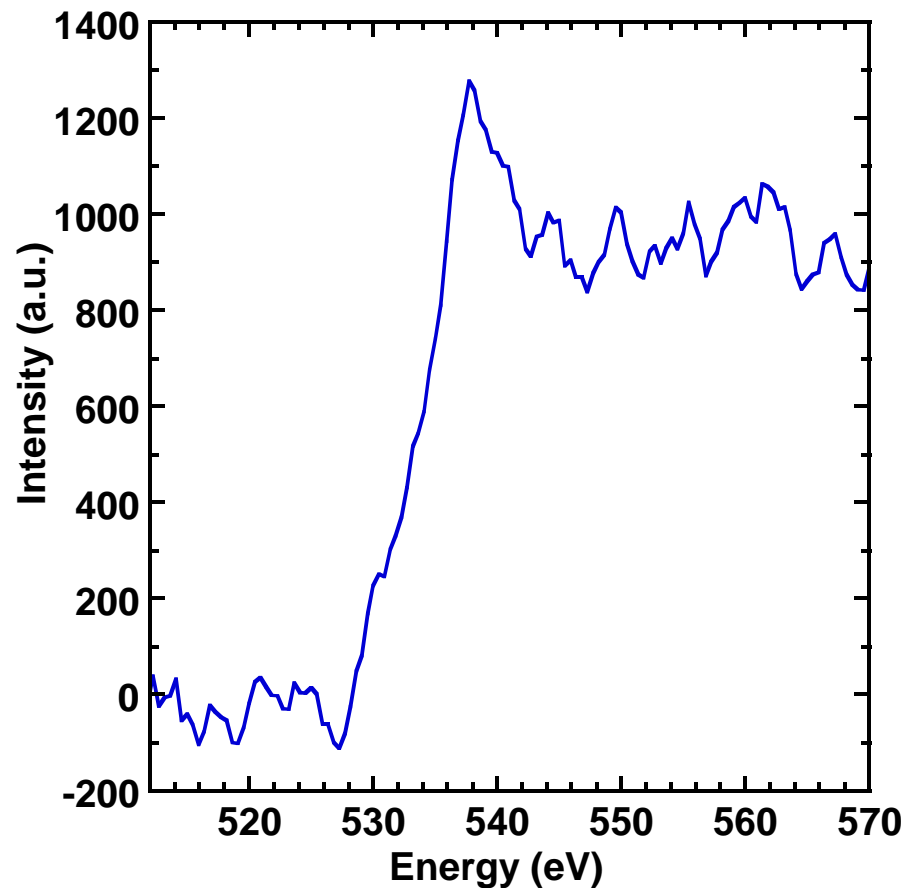
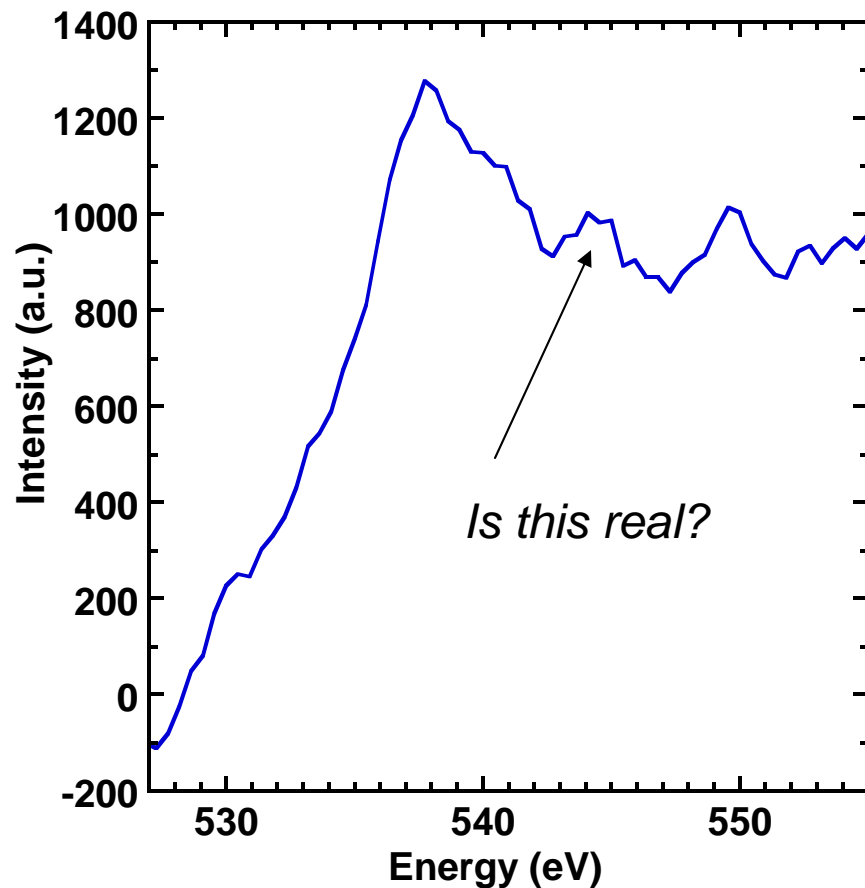
- *Condenser < Objective Aperture*
- *Thickness fringes*
- *Fresnel Contrast*

Incoherent Illumination:

- *Condenser > Objective Aperture*
- *Diffraction contrast suppressed*

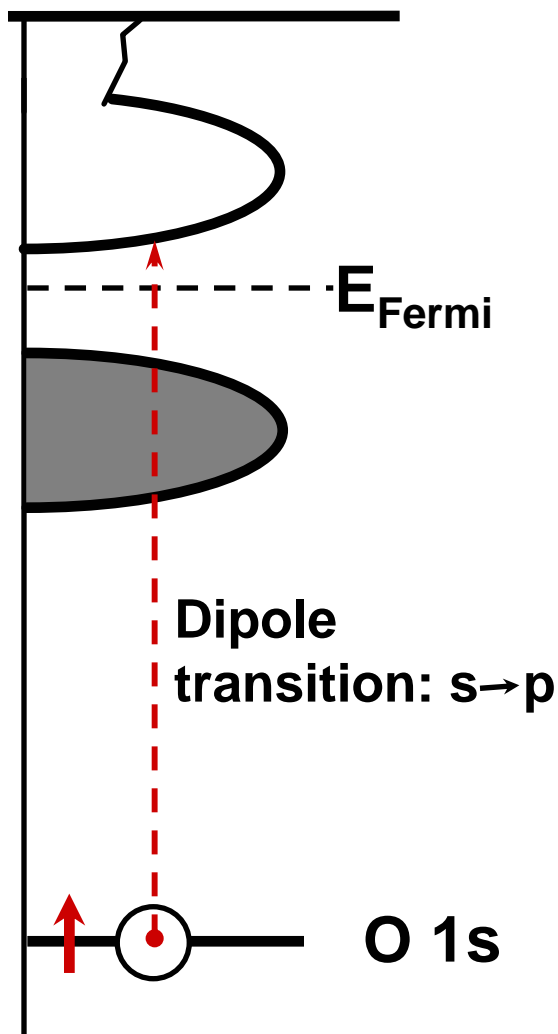


Interpreting Experimental Data



*Always show the pre-edge background.
Gives noise level & confidence in background subtraction*

Core-Level *Electron Energy Loss Spectroscopy*



EELS measures a **local density of states** partitioned by

- **site** - as the probe is localized,
 - **element** - the core level binding energy is unique
- probes the conduction band
 - provides local electronic information

EELS Theory



In the first Born approximation, the partial cross section for the inelastic scattering of an electron wave packet (with initial group velocity v), undergoing a momentum transfer \vec{q} and losing energy E ,^{58–60} is given by

$$\frac{d^2\sigma(E, q)}{dE dq} = \frac{8\pi e^4}{\hbar^2 v^2} \frac{1}{q} \sum_{i,f} |\hat{\epsilon}_q \cdot \langle f | \vec{r} | i \rangle|^2 \delta(E - E_f + E_i) + \dots$$

*Some subtleties as to which density of states is measured
see Muller, Singh and Silcox, Phys Rev **B57**, 8181 (1998)*

*This is very important if you want to measure charge transfers
(you don't – there is no unique definition).*

Dipole selection rules: $\Delta l = \pm 1$, $\Delta j = 0, \pm 1$

K-edge: $1s \rightarrow p$ L-edge: $L_1 : 2s \rightarrow p$; $L_{2,3} : 2p \rightarrow d, s$;

EELS as a Local Density of States (LDOS)



If we project the total density of states on to a local set of states and examine the overlap of each eigenstate $|n, \vec{k}\rangle$ with the local state $|i\rangle$. The probability of finding an electron in the eigenstate $|n, \vec{k}\rangle$ at site $|i\rangle$ is $|\langle i | n, \vec{k} \rangle|^2$ so the local contribution to the density of states from site $|i\rangle$ is

$$n_i(E) = \sum_{n, \vec{k}} |\langle i | n, \vec{k} \rangle|^2 \delta(E - E_{n, \vec{k}}),$$

and the charge associated with the local state $|i\rangle$ is

$$\rho_i = 2 \int_{-\infty}^{E_F} n_i(E) dE,$$

The basis set chosen for $\{|i\rangle\}$ is not unique, so the amount of charge at site i is also not Unique. (e.g. a sphere of arbitrary size).

For EELS, the oscillator strength

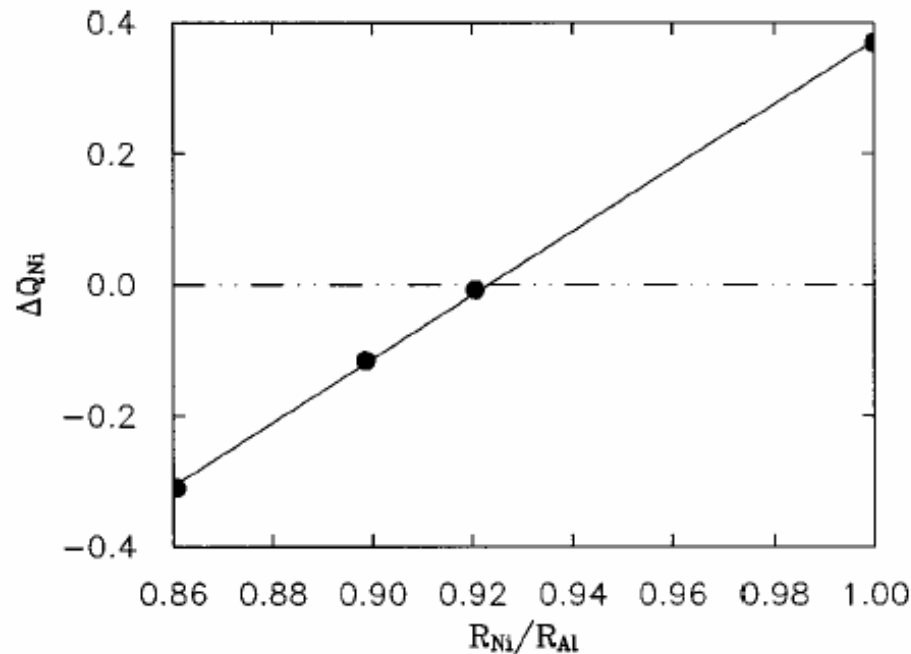
is proportional to a LDOS with a basis set of $r|\phi_c\rangle = |r\phi_c\rangle$ where ϕ_c is the initial core state, $|i\rangle$

$$F(E) \propto \sum_{all f} |\langle r\phi_c | f \rangle|^2 \delta[E - (E_f - E_c)].$$



Don't compare EELS to calculations of charge transfer

The charge-transfer problem: Since there is no unique definition of a local density of states, there is also no unique definition for charge transfers between local states



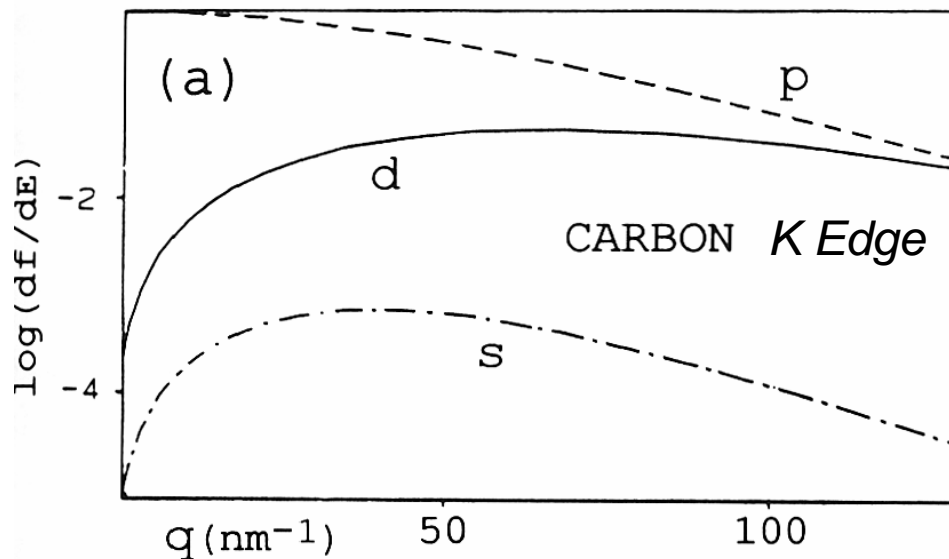
- To caution against directly comparing EELS “whitelines” against calculated charges, we show the charge transfer from an atomic sphere surrounding a Ni atom in the *B2* NiAl compound, calculated in the LMTO-ASA approximation.
- The choice of the relative sphere sizes for the Ni and Al sites are a matter of computational convenience, rather than being a physically measurable property of the system.
- By altering the ratio of the Ni/Al sphere sizes we can change not only the magnitude, but also the sign of the Ni-Al charge transfer.

*Muller, Singh and Silcox, Phys Rev **B57**, 8181 (1998)*

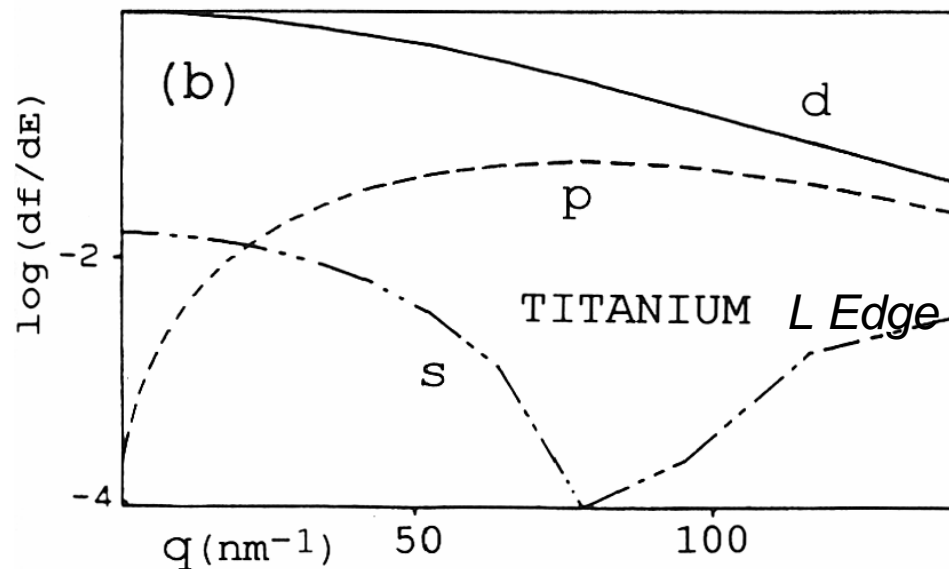


Dipole Approximation is good for Core Level EELS

(except when the probe < core orbital size – can happen during channeling)



1s→p dipole
1s→s monopole
1s→d quadrupole

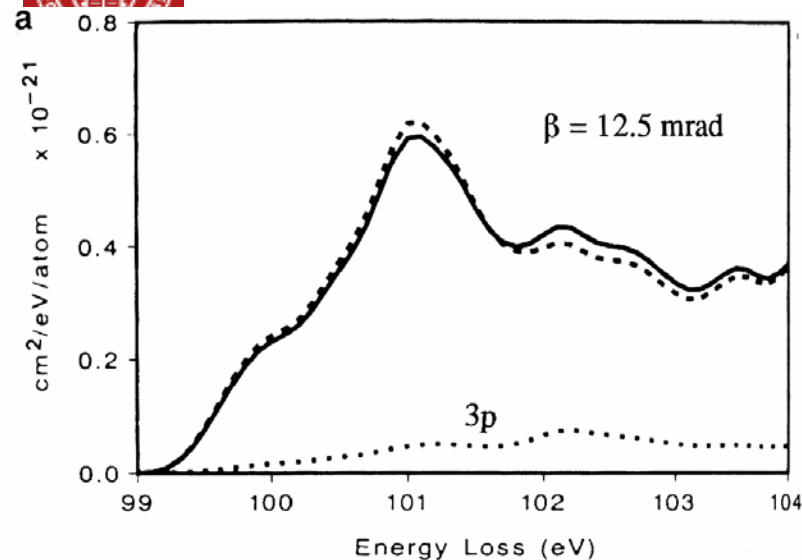


2p→d dipole
2p→p monopole
2p→s dipole

Dipole Approximation is good for Core Level EELS

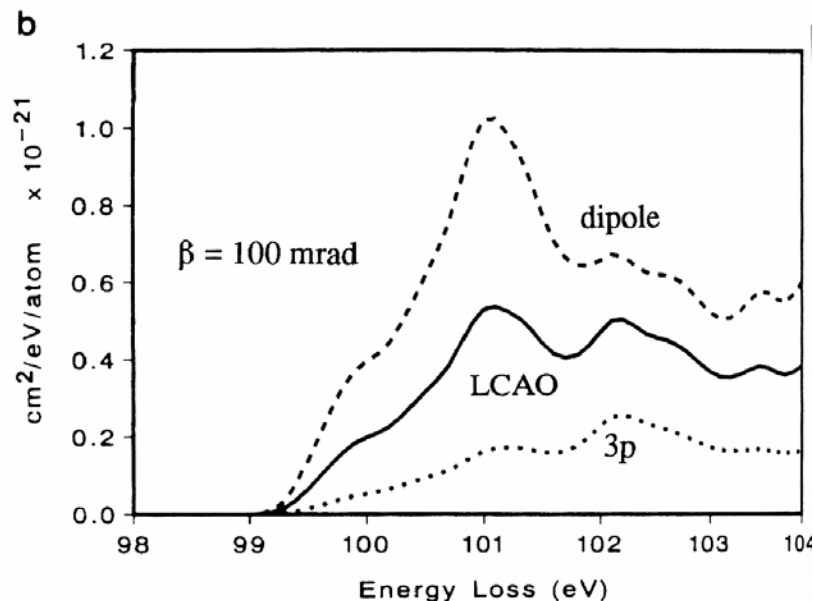


Si L_{23} edge for a 100 keV incident electron



Collection angles of 12.5 mrad ($q=20 \text{ nm}^{-1}$),

The solid line is the full calculation, the dashed line is the dipole contribution, and the light dotted line is the nondipole 2p-3p term

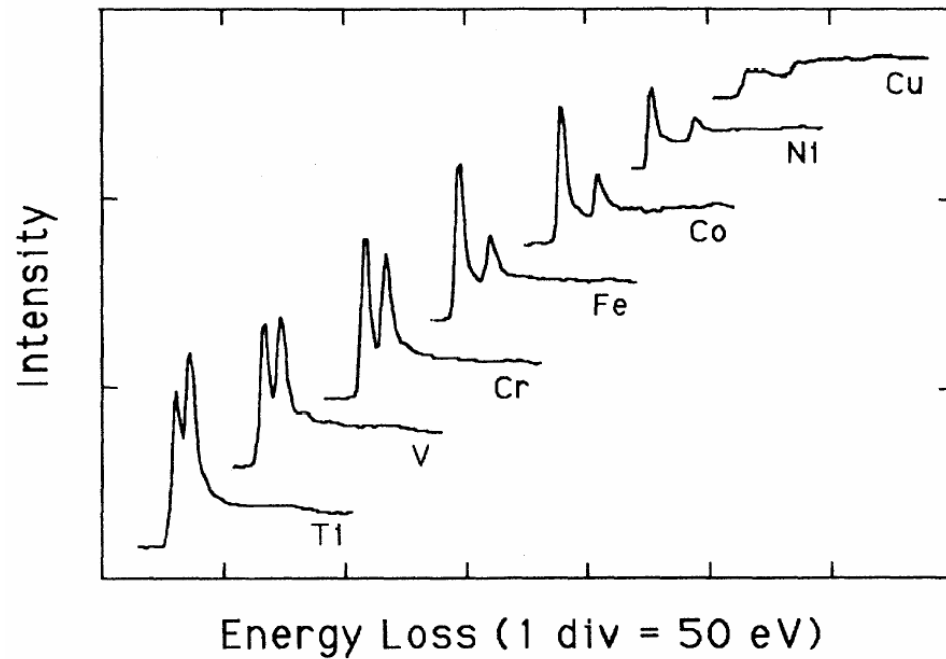


Collection angles of 100 mrad ($q= 167 \text{ nm}^{-1}$)

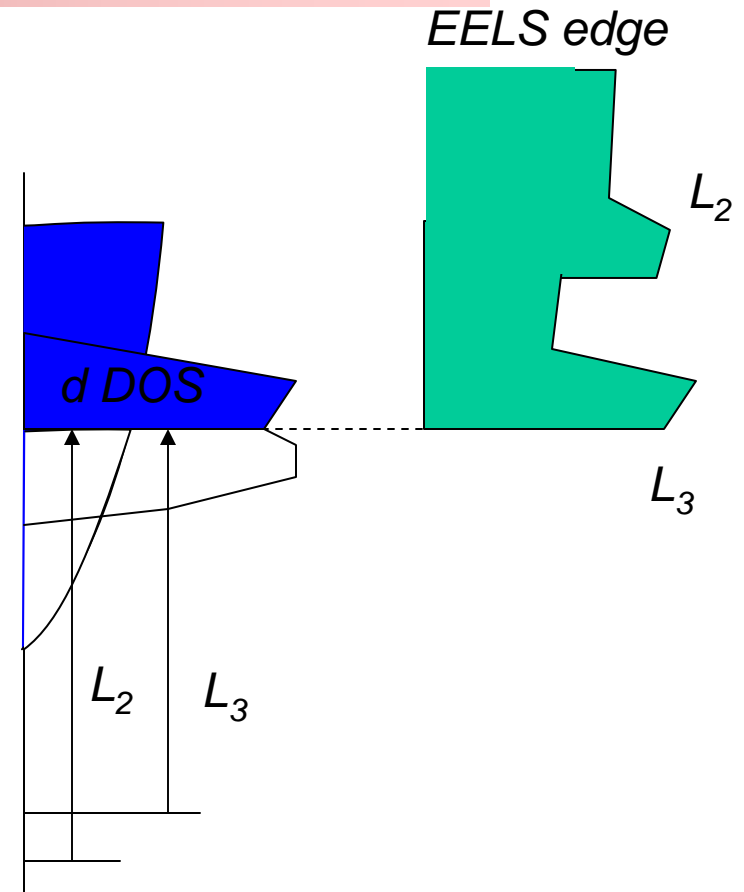
EELS Fine Structure of Transition Metals



Ground state interpretation of spectra as a LDOS (ignore core hole)



Pearson, Fultz and Ahn, *Phys Rev B* 47 (1993)

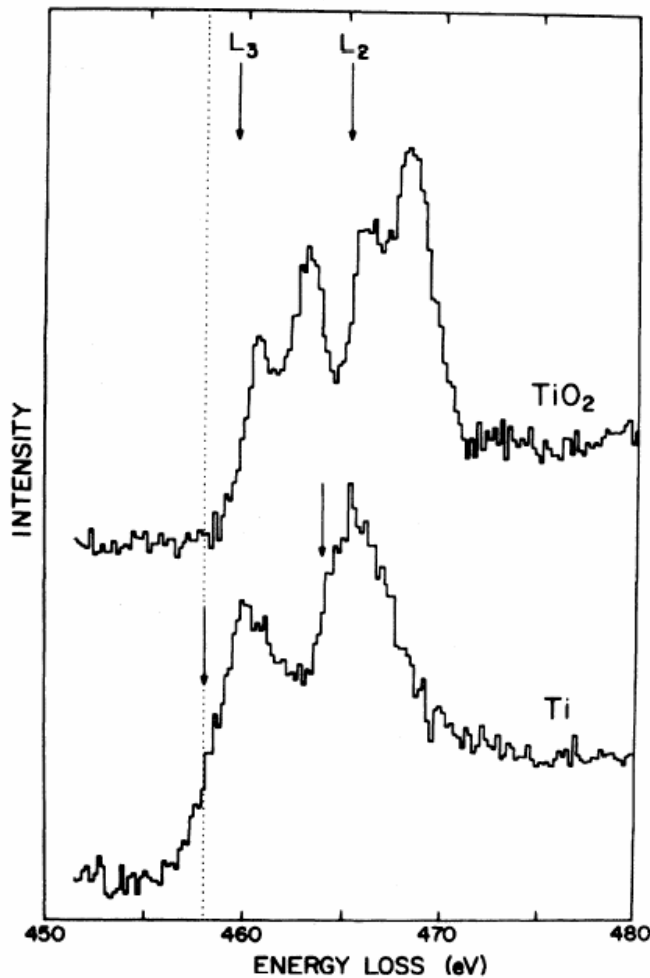


EELS Fingerprints of Oxidation States

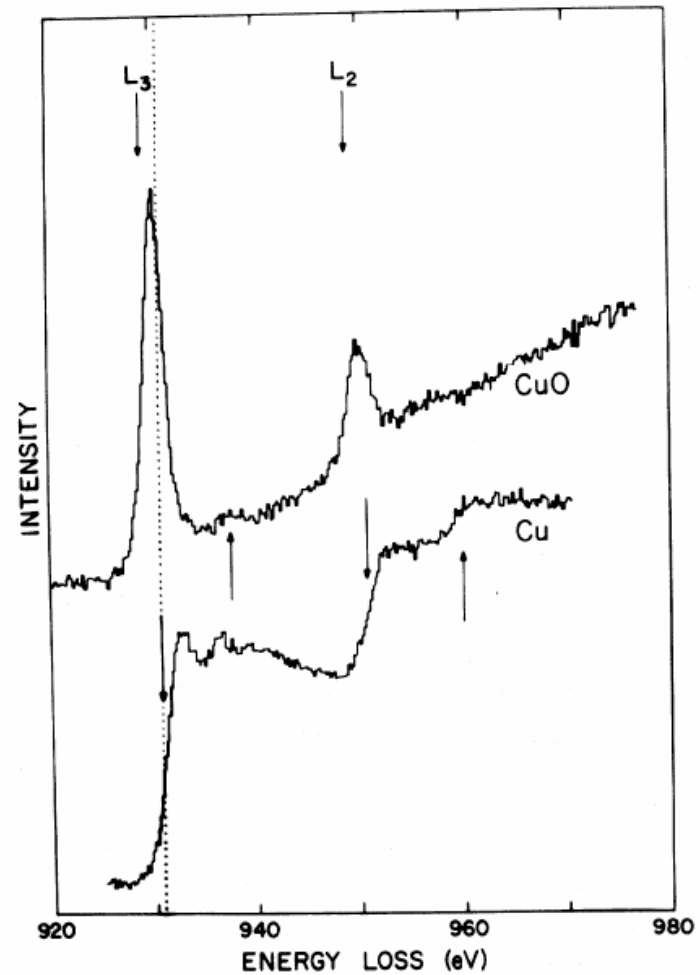


Leapman, Grunes, Fejes, *Physical Review* **B26** 614-635 (1982)

Ti $L_{2,3}$ Edge



Cu $L_{2,3}$ Edge





Fingerprint EELS from our website

www.weels.net : EELS spectra of common semiconductor materials

Welcome to WEELS : Webservice for Electron Energy Loss Spectra

Instructions: Element boxes that contain hyperlinks link to reference spectra. Click on the element of interest

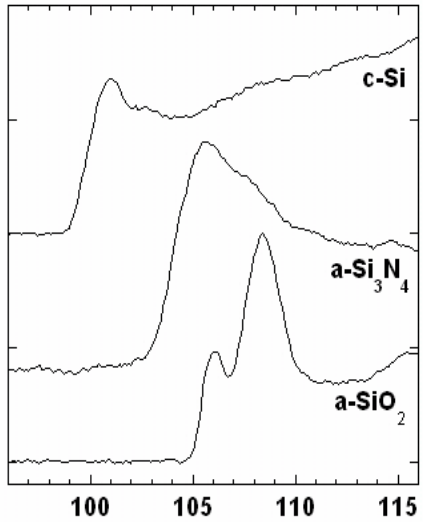
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H																	2
3 Li	4 Be																
11 Na	12 Mg																
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	{57-70}	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At
87 Fr	88 Ra	{89-102}	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Uuu	112 Uub	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus

Identify the local environment from the shape of the spectrum

(e.g. Cu vs. CuO vs. Cu₂O)

Spectra for

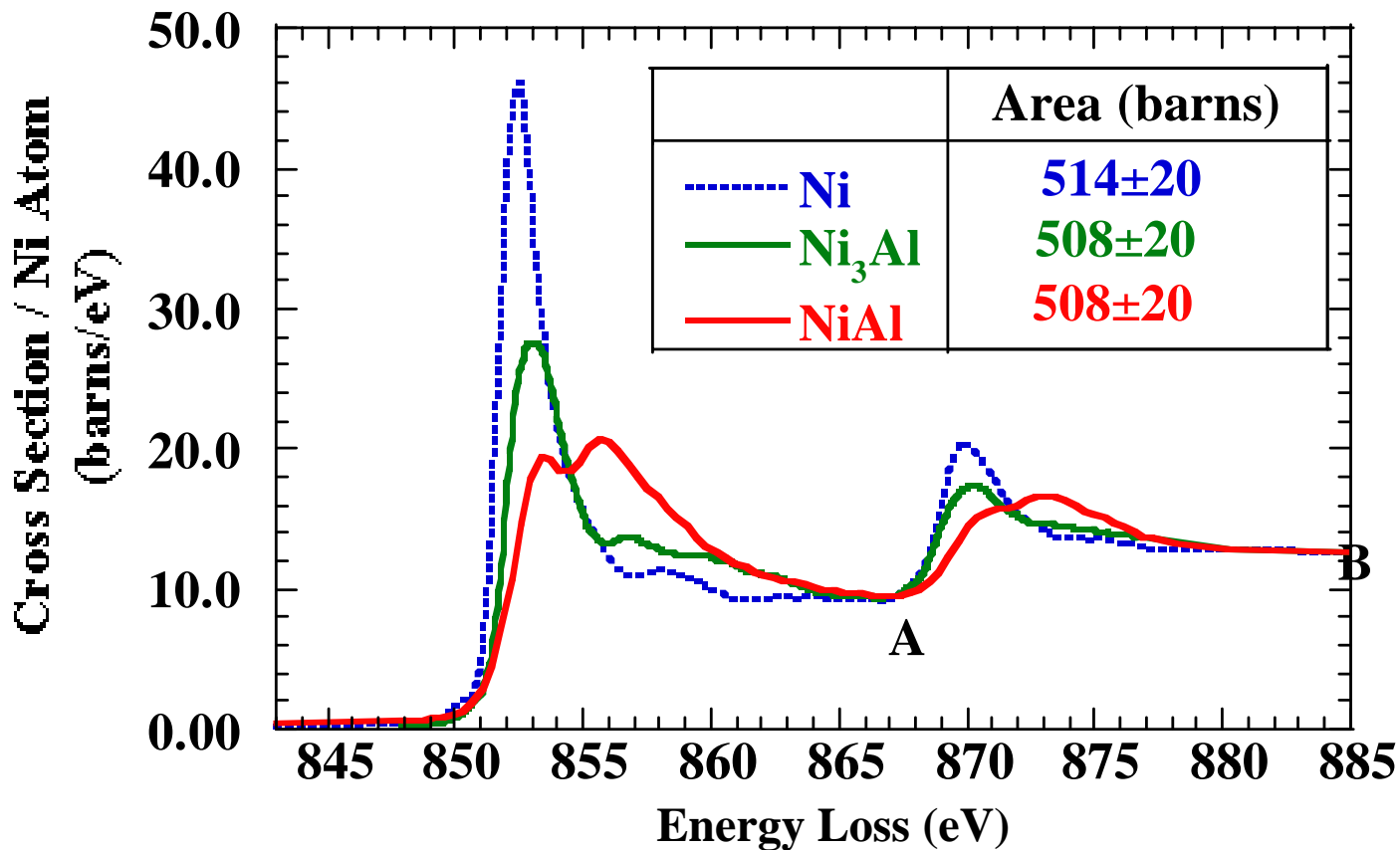
- [Silicon bulk](#)
- [Silicon in N-Blok material](#)
- [Silicon in Silicon Carbide \(SiC\)](#)
- [Silicon, Si₃N₄ and SiO₂](#)
- [Silicon in oxynitride \(SiON\) and Silicon Di-](#)

Spectrum	Comments
	By: Aycan Yurtsever and Peter Ercius @ Cornell University Microscope: VG HB 501UX STEM Energy Resolution: 0.5 eV

What Happens when Al is added to $\text{Ni}_x\text{Al}_{1-x}$?



Ni $L_{2,3}$ Edge After Deconvolution with Low Loss

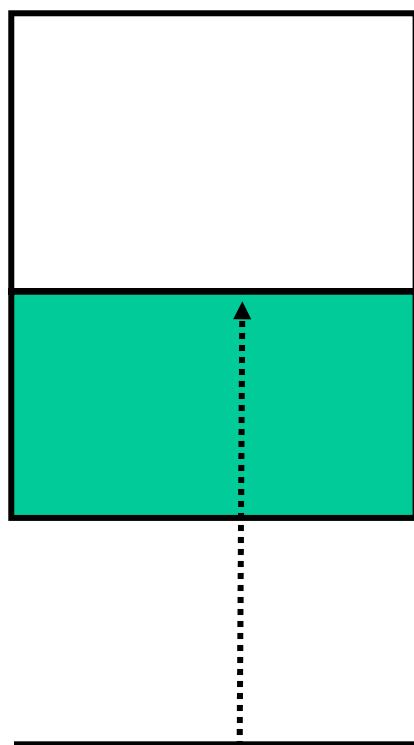


- The Total Areas under each curve are very similar (no charge-xfer).
 - Ni d is broadened, shifting states from the main band, to the tails
- increased Ni-Al bonding (Ni p-d hybridization)

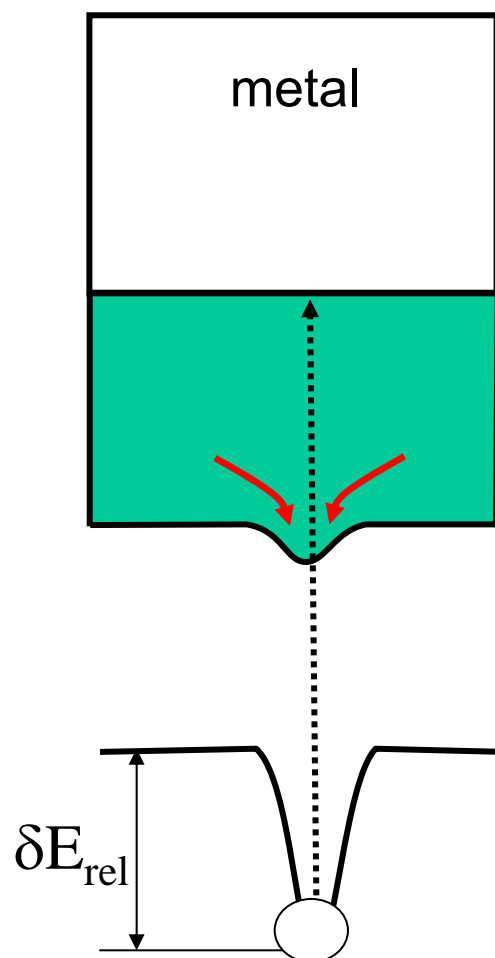


EELS: Final State Effects

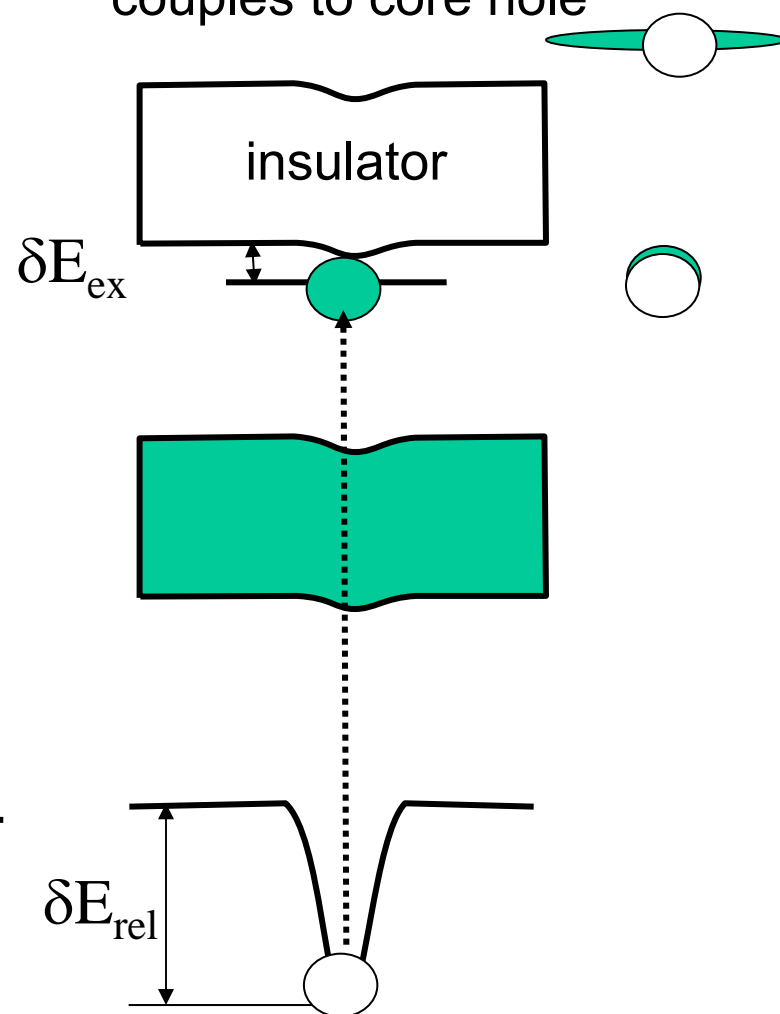
Initial State



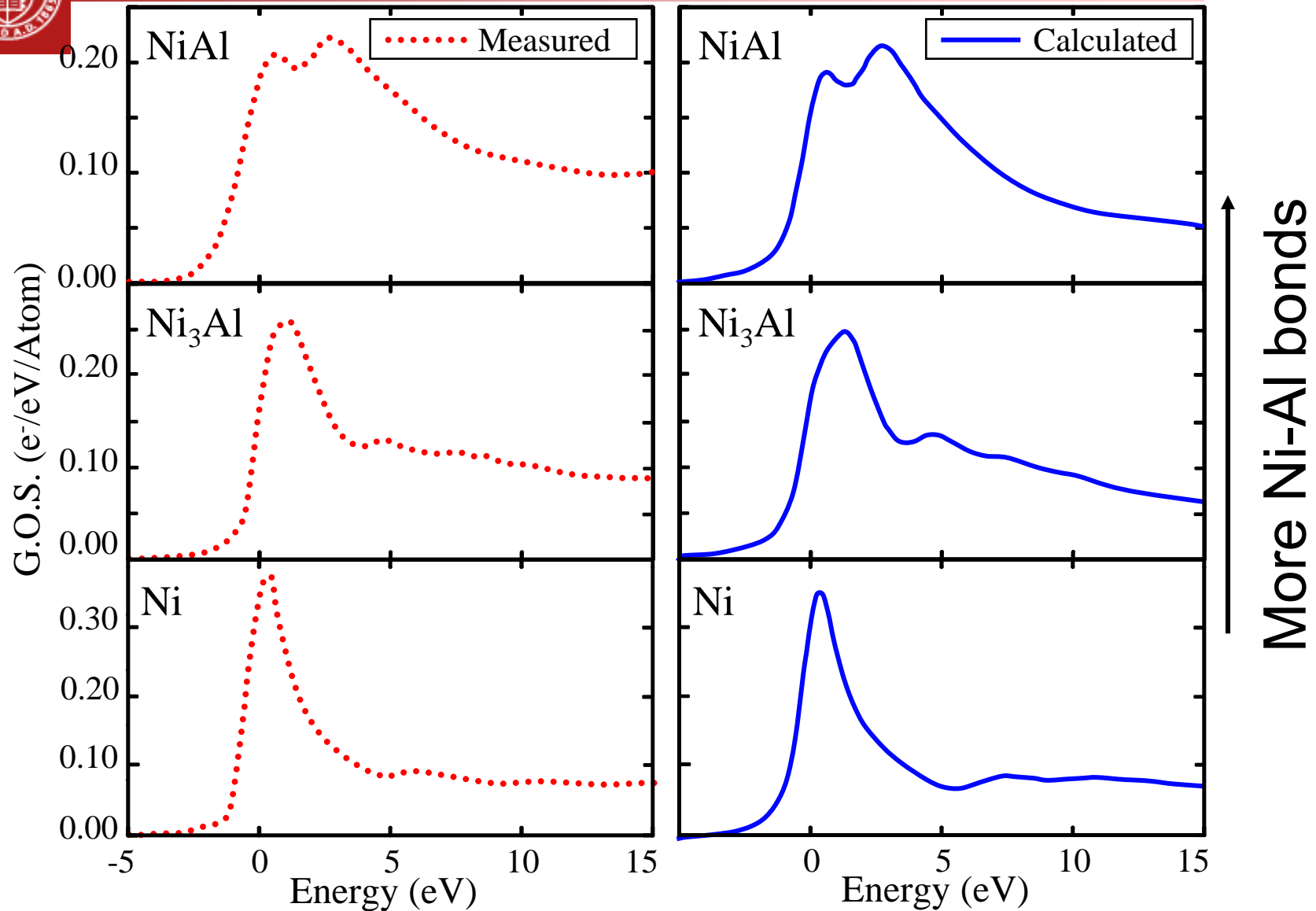
Electrons relax to screen core hole



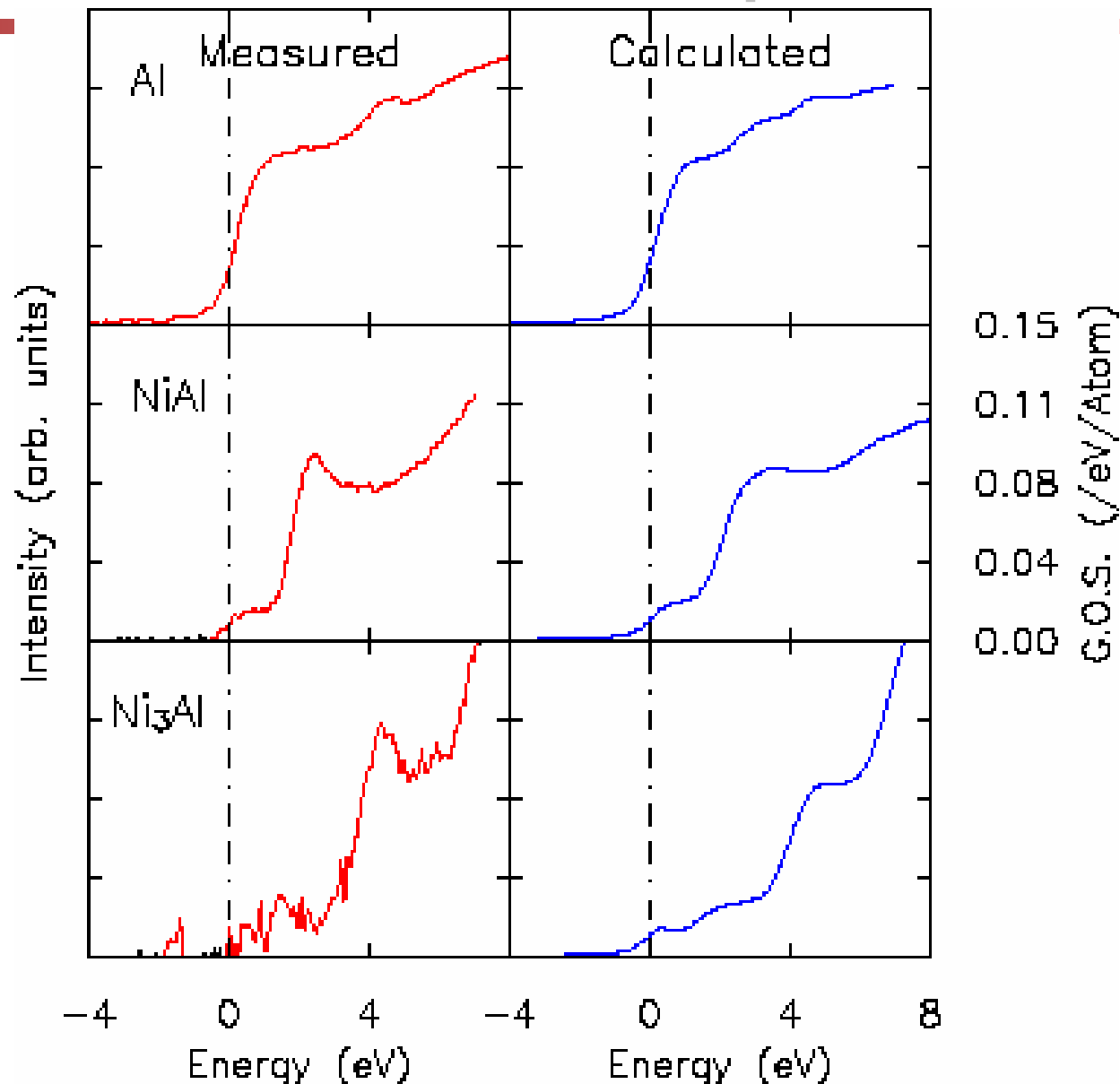
Excited electron couples to core hole



Comparison of the Ni L_3 Edge measured by EELS with the calculated, unoccupied d DOS of Ni



Comparison of the Al L_3 Edge measured by EELS with the calculated, unoccupied GOS of Al

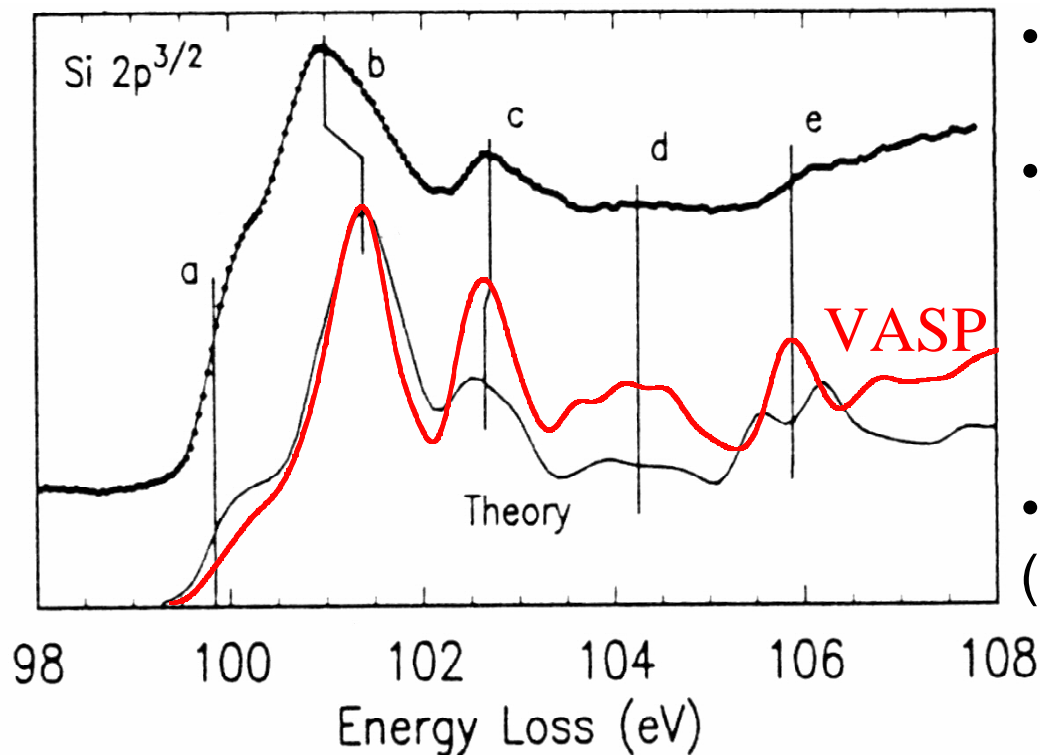




Ground State Theory: the Si L_3 Edge

X. Weng, P. Rez, P. E. Batson, *Sol. Stat. Comm.* **74** 1013 (1990).

(PAO calculation with 0.3 eV broadening)

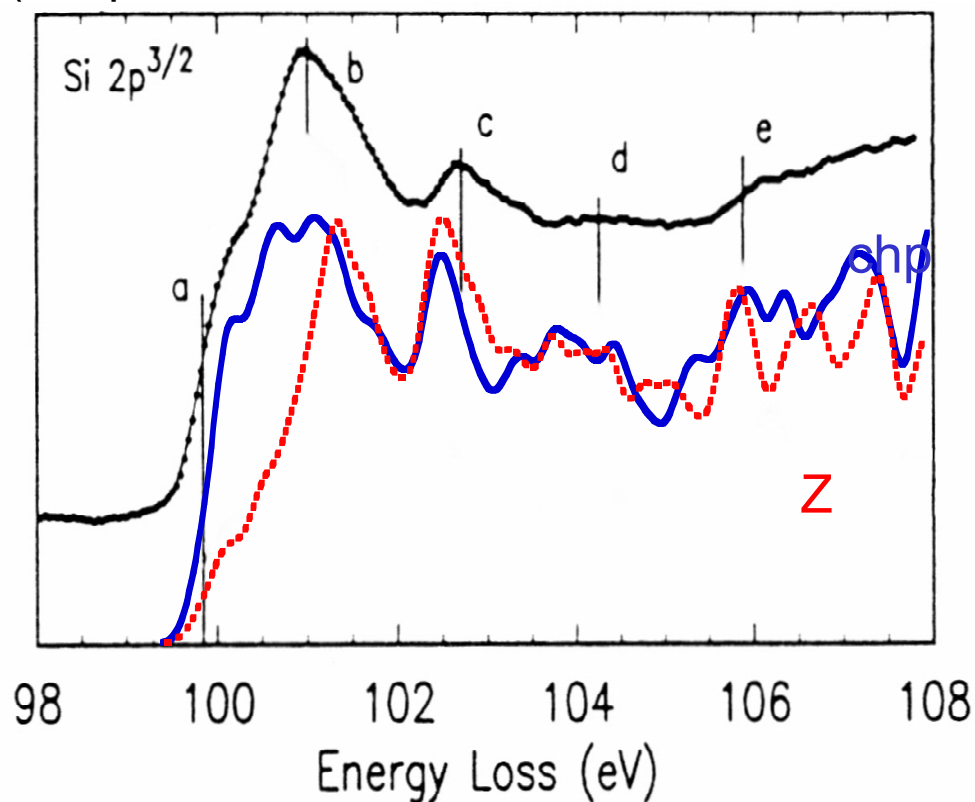


- Weng aligns theory at edge onset
- All major features present, but
 - peak a is too weak
 - peak b is too high
 - c, d, e are in good agreement
- PAO results reproduced by VASP (using s/d = 1.1)



Excited State Theory: the Si L_3 Edge

(Adaptive coordinates calculation with 0.3 eV broadening, core hole in 64 atom cell)

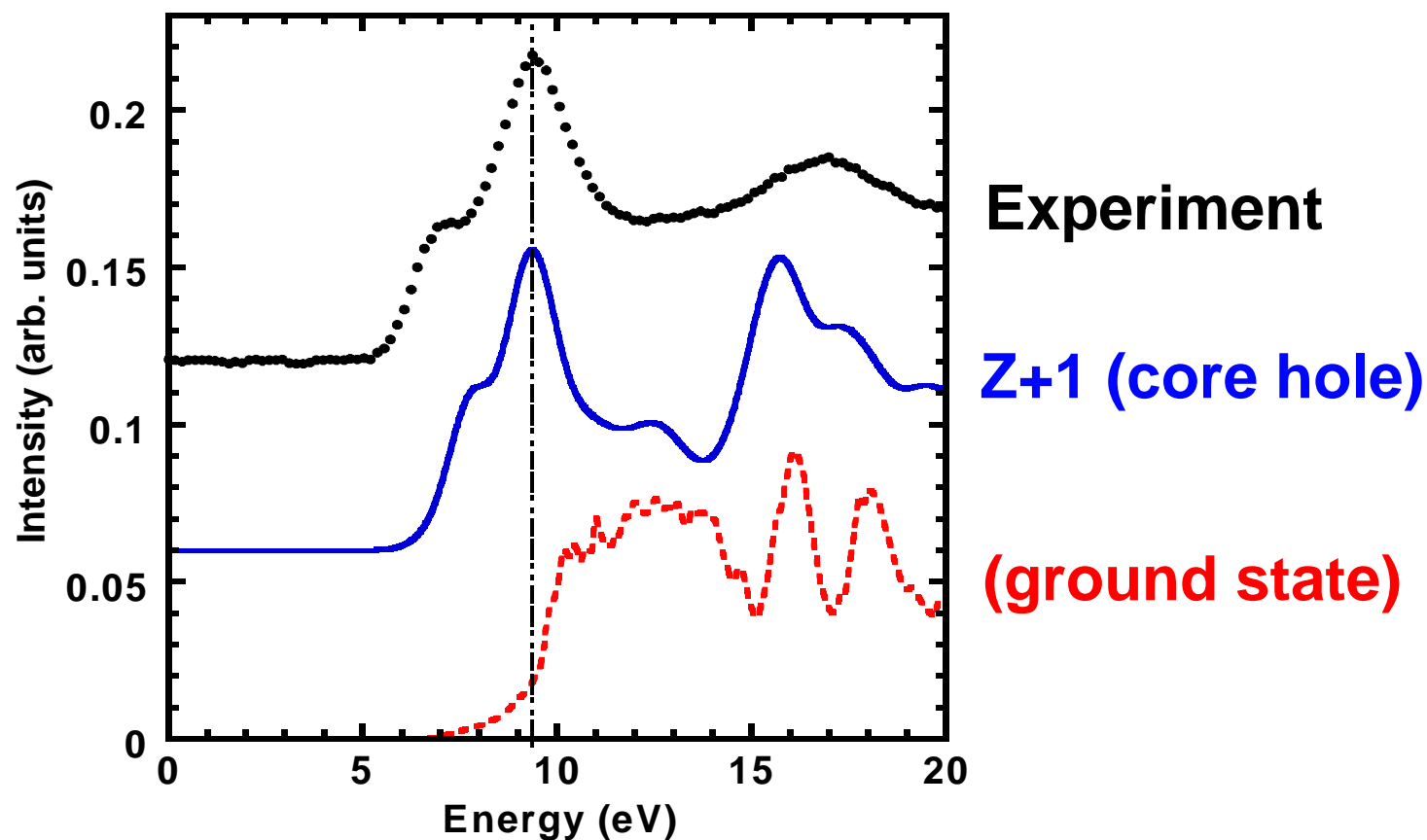


- align theory at edge onset
- ch: All major features present, but
 - peak a is too high
 - peak b is split, too wide
 - peak d is too sharp
- Only difference from ground state is in the first 1eV

Core hole in Si does not add new features at 0.3eV, just sharpens old ones



Comparison of the Measured Si-L Edge with ab-initio Calculations

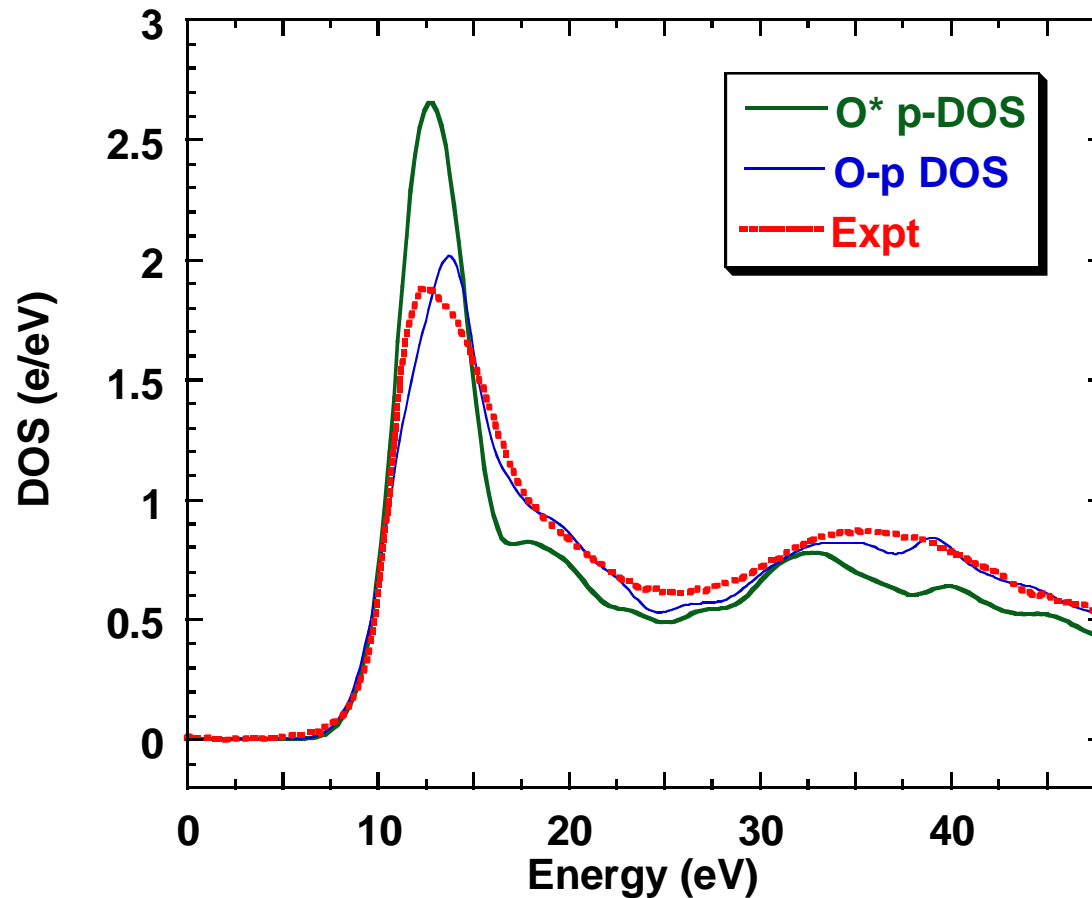


Strong core-hole effects on the silicon-L Edge
(it does not reflect the ground state)

Neaton et al, Phys. Rev. Lett. **85** 1298(2000)



Comparison of the Measured Oxygen-K Edge with *ab-initio* Calculations



Inclusion of a core-hole effects
overestimates the influence of the exciton



When are core holes important?

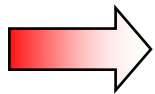
- *When you have good energy resolution (<1 eV)*
- *When screening is poor*
 - *Metals (small), semiconductors (medium), ionic (huge)*
 - *The effect is larger on anions than cations*
 - *More noticeable in nanoparticles and clusters than bulk*
- *Batson's Rule: core hole effects are more pronounced when the excited electron is confined near the core hole. (It shouldn't work, but it does.)*
 - *Atoms surrounded by strong scatterers (often nodeless valence wavefunctions 1s, 2p, 3d...) (e.g Si in SiO_x, Al in NiAl, TiB₂ out of plane)*

Limits of Density Functional Theory (DFT)



A practical matter:

- The theory provides total energies for the ground state and (with constraints) also the energies for excited states.
- One total energy per calculation (minutes → days)
- Core level binding energy $E_b = E_{excited} - E_{ground}$ (a difference of 2 total energies)
- A full EELS spectrum needs 1 total energy per excited state ($\propto E^3$) **YEARS!**



We use approximate methods instead (1 calc. per spectrum)

Need to understand errors in DFT in order to produce effective approximations

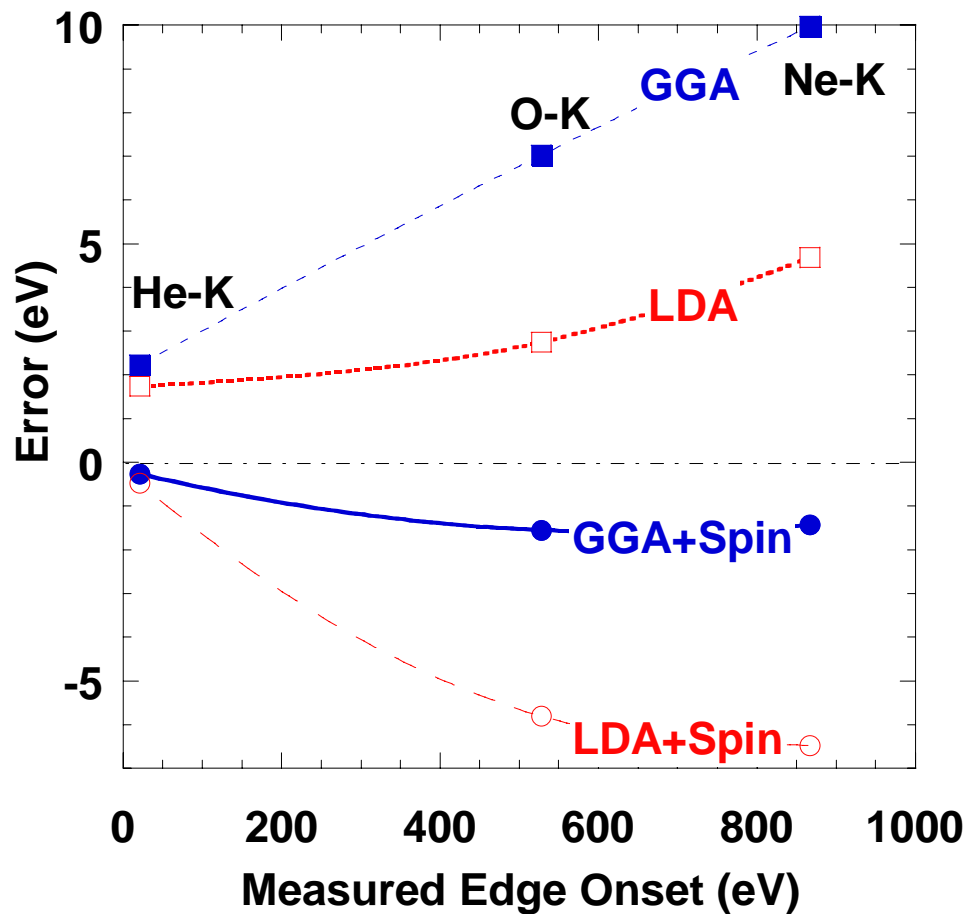
- which errors are large, which will cancel?
- Use EELS binding energies to study systematic errors

A DFT Test Case: Noble Gas Edge Onsets



Total Energies from GGA: $E_b = E_{\text{excited}} - E_{\text{ground}}$

GGA (generalized gradient approximation) is more accurate than LDA, but still:



- LDA, no spin: 1% error
- LDA+spin : -1% error
- GGA + Spin : 0.1% error
(~ 0.5 eV at O-K edge)

Why spin?
*Less self-interactions
in localized core hole*

More localized the core hole, the bigger the error



LDA vs. “Exact” Eigenvalues

The real excitations of the system obey the Dyson equation:

$$\left\{ -\frac{1}{2} \nabla^2 + V_c(r) \right\} \psi(r) + \int \psi(r) \Sigma(r, r', E) \psi(r') dr' = E \psi(r)$$

Self-energy

The local density approximation (LDA) replaces $\Sigma(r, r', E)$ with $\Sigma(r)$

(LDA eigenstates are fictitious constructs to solve the Kohn-Sham equations)

$\Sigma(r, r', E)$	$\Sigma(r)$	Effect of LDA on Eigenvalues
complex	real	No lifetime broadening
Non-local	local	Problems with changing densities
<i>Energy-dependent</i>	<i>Energy-independent</i>	<i>Band gap & shape of DOS are wrong!</i>

➡ LDA DOS (Z, Z+1, all-electron) cannot rigorously describe EELS

A Physical Interpretation for LDA Eigenvalues

(LDA eigenvalues e_i do not reproduce the true quasiparticle excitation spectrum)

Instead:
$$\frac{\partial E_{Tot}}{\partial n_i} = e_i$$

Taylor Series Expansion of the EELS excitation from state i to f

$$\Delta E_{i \rightarrow f} = e_f - e_i + F_{i,f} + \Pi_{i,f} + \dots$$

← “relaxation energy”

Hartree Energy: $F_{i,f} = \iint \rho_i(r) \rho_f(r') / |r - r'| \, dr dr'$ (short ranged, will compress DOS)
(~10%)

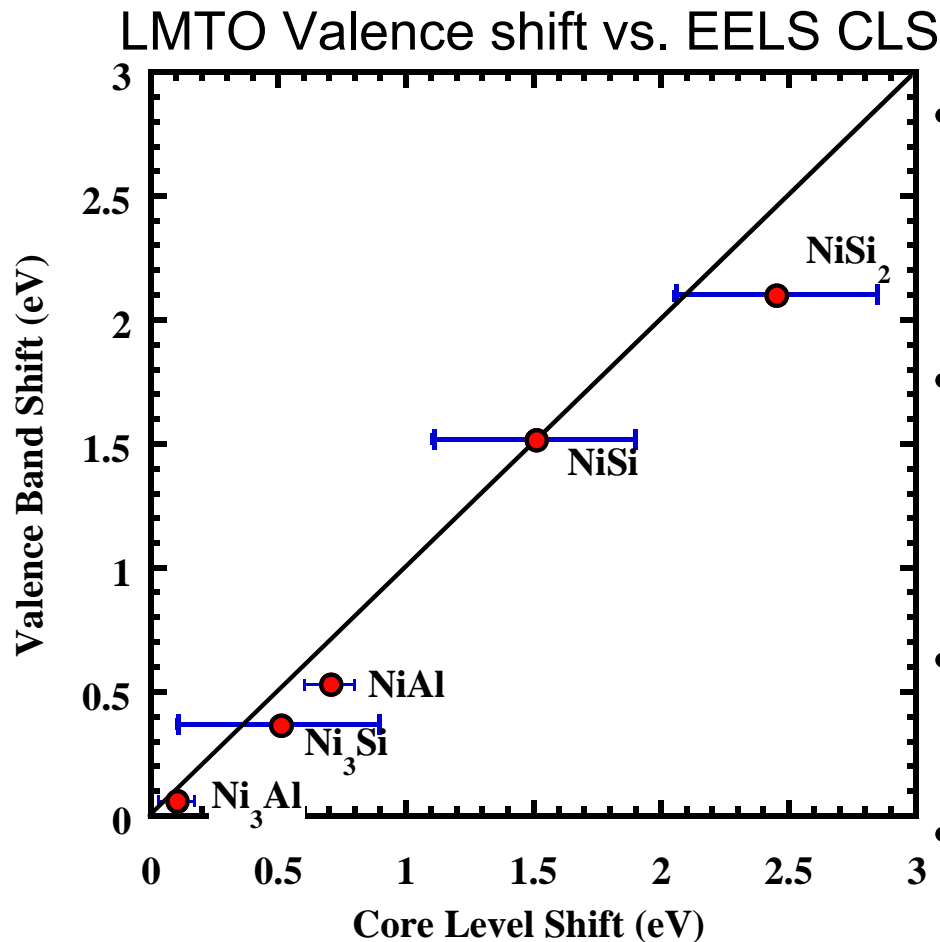
Self-interaction: $\Pi_{i,f} = \int dr \, \rho_i \rho_f \left(2(\partial/\partial \rho) \epsilon_{xc}[\rho] + \rho (\partial^2/\partial \rho^2) \epsilon_{xc}[\rho] \right)$ (slowly varying)
(~2%)

Core level shift = eigenvalue difference + “relaxation energy”

In Metals the Core Level Shift tracks the eigenvalue shift



WHY?



- A Valence band shift
→ changed electrostatic potential
- Core levels experience a similar electrostatic potential
→ a similar shift in binding energy
- Most accurate for nodeless valence states (1s, 2p, 3d, 4f)
- (Only true for metals - no gap)

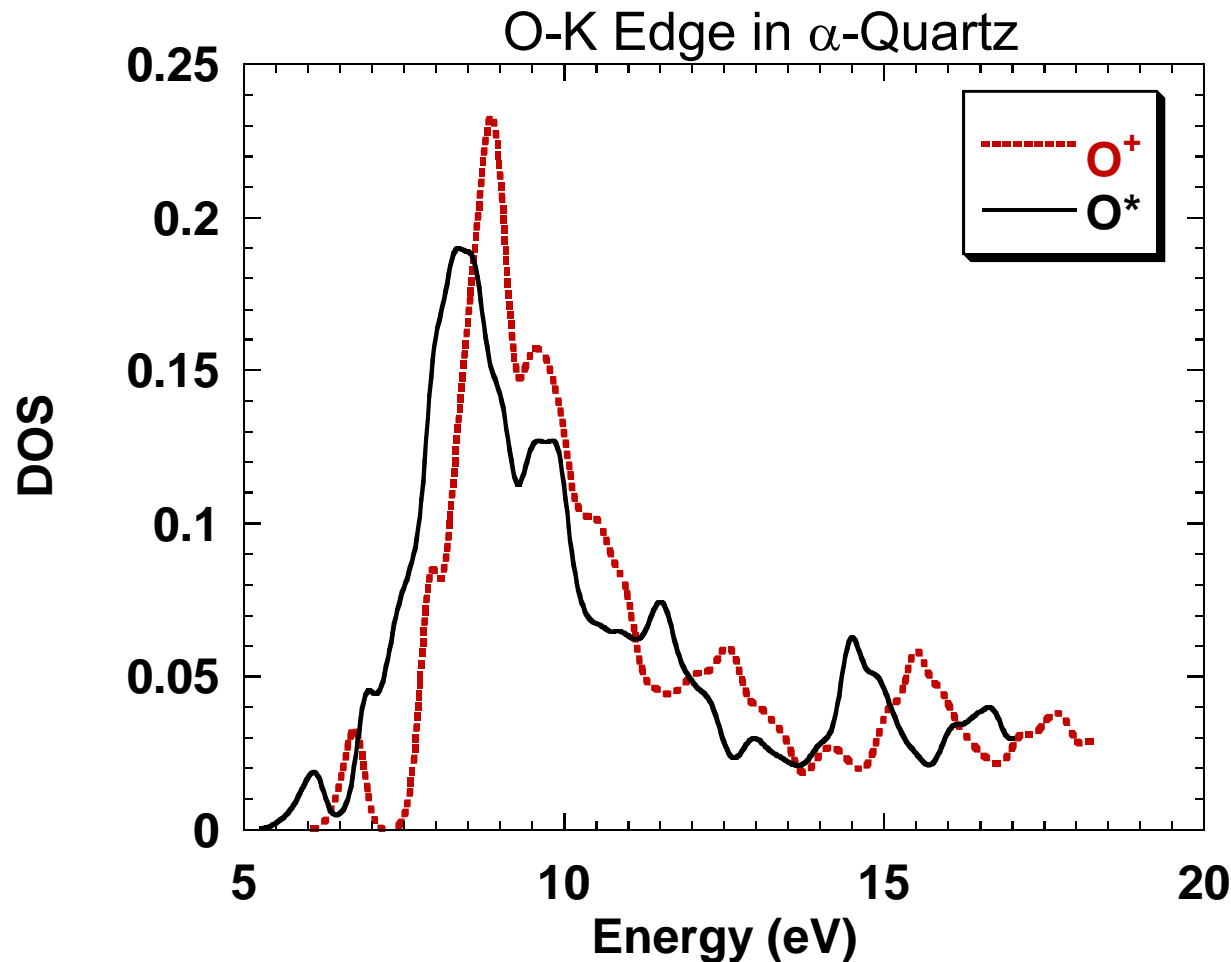
Core level shifts can tell us about the occupied, valence bands!

[D. A. Muller, *Ultramicroscopy* **78** (1999) 163]

How Big is the Hartree Correction?



Localization of the Ejected Electron alters the Spectrum



O^* : Excited e^- is localized at edge onset.

- Largest overlap with core
- Largest Hartree energy

O^+ : Excited e^- is delocalized throughout conduction band

- Small overlap with core
- Small Hartree correction

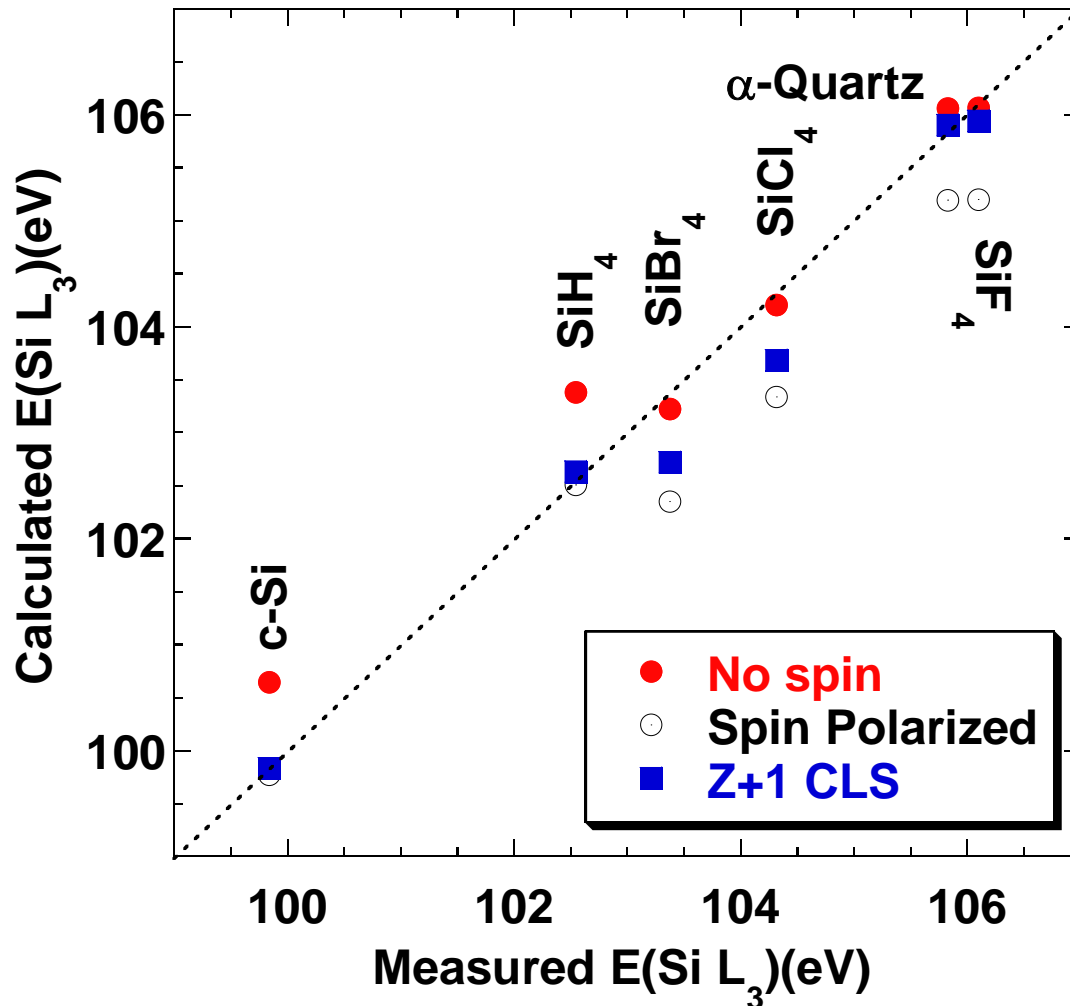
→ Spectrum is stretched
~ 2 eV

Cannot describe excitation quantitatively with 1 self-consistent calculation

Core Level Pseudopotentials: $Si L_3$



(include the core hole in pseudopotential: easy to model large systems)



- Spin polarization is important (~ 0.9 eV correction)

- pseudopotential error increases with ionicity difference from the free atom.

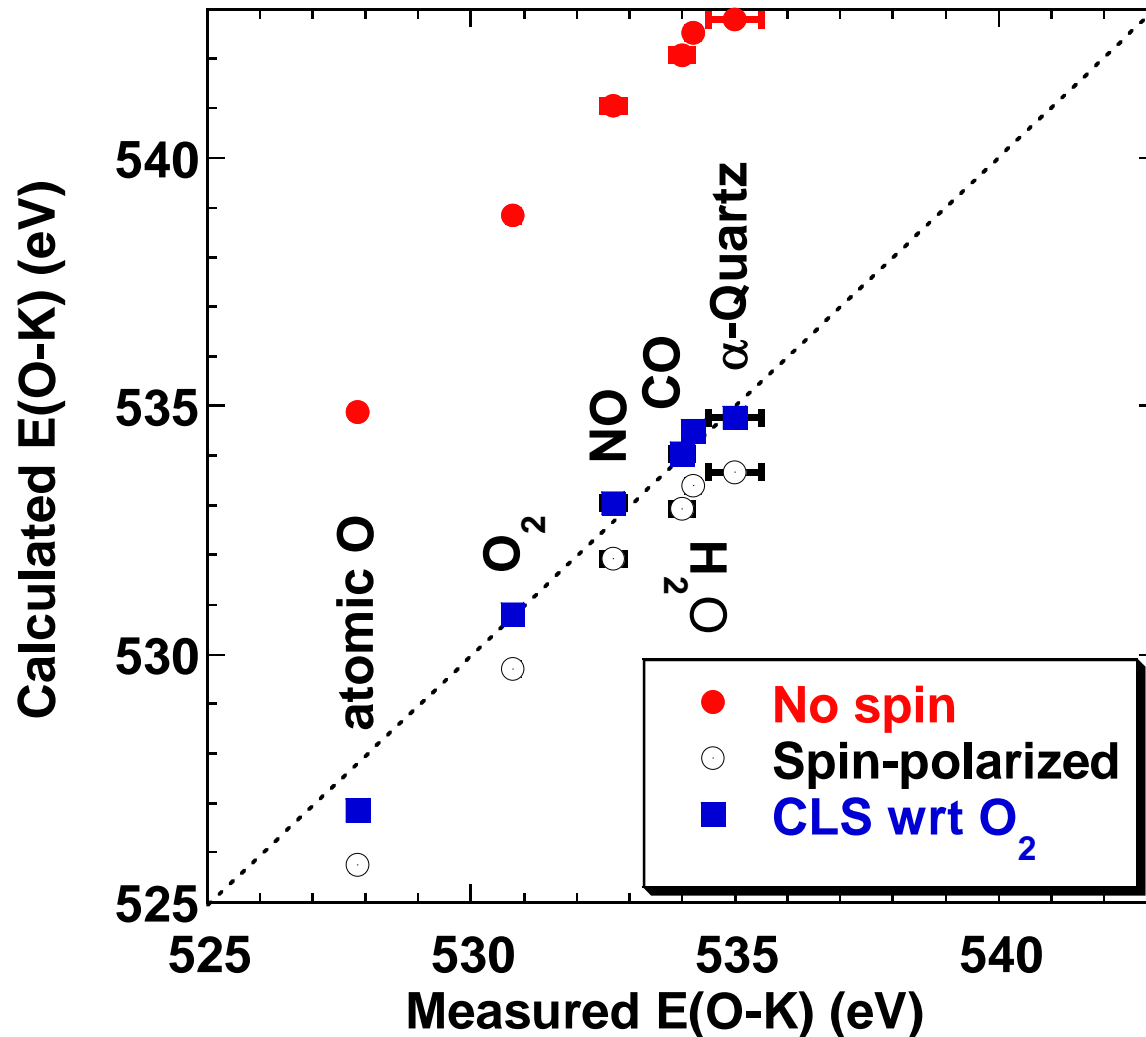
- (Z+1) total energy differences are as accurate

➡ Si core hole has the same energetics as a P impurity

Core Level Binding Energies: O-K



(Total Energy GGA calculations - more accurate than LDA)



- All published E_B LDA calcs to date neglect spin.

- No spin: 8 eV error !

Absolute Error in DFT ~ 0.5 eV



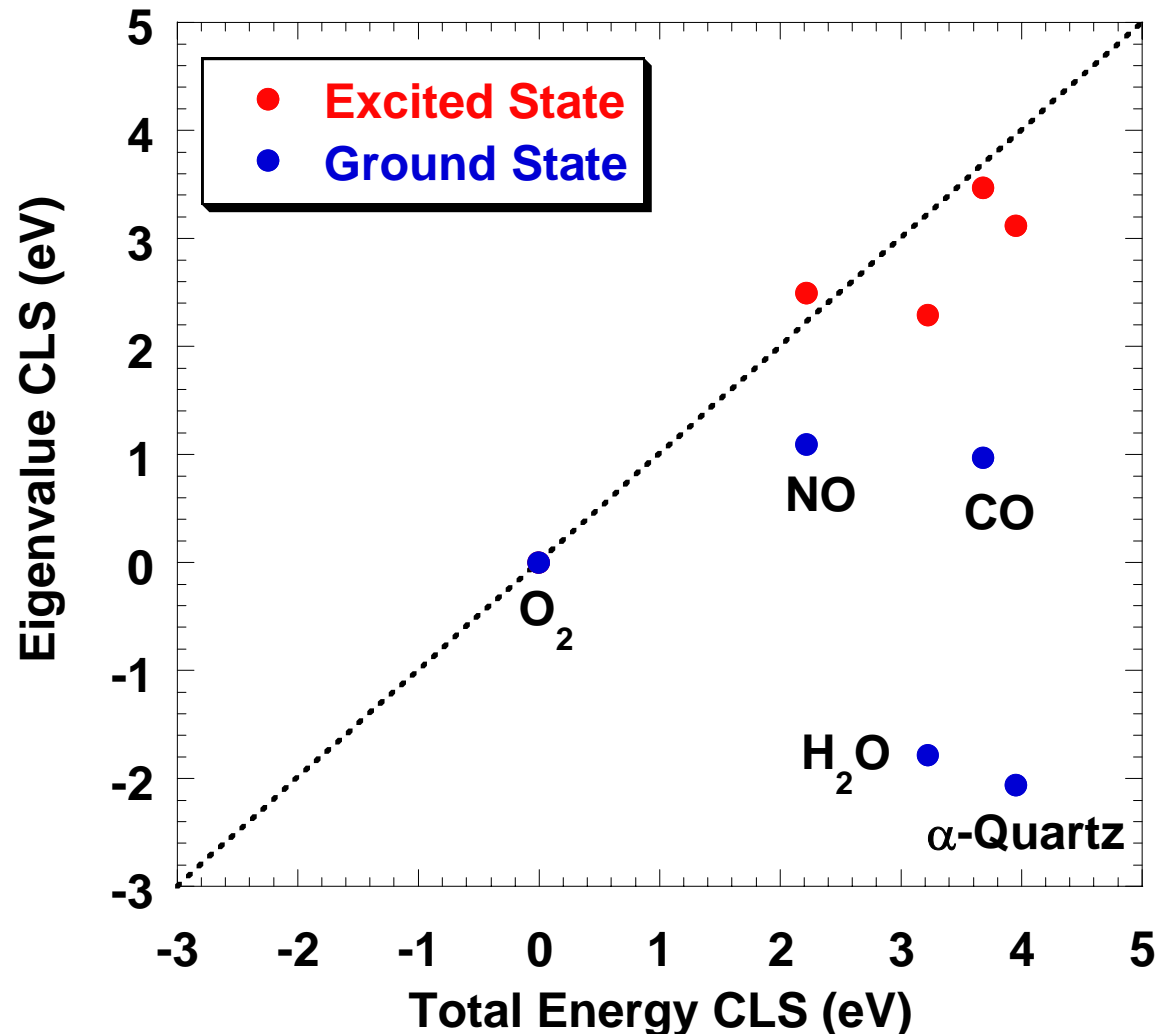
Core level shifts are still more accurate than absolute values



Core Level Shifts in Insulators

(Bandgap will introduce errors ...)

O-K Edge CLS vs Eigenvalue differences $D(e_{CB} - e_{2s})$ wrt O_2

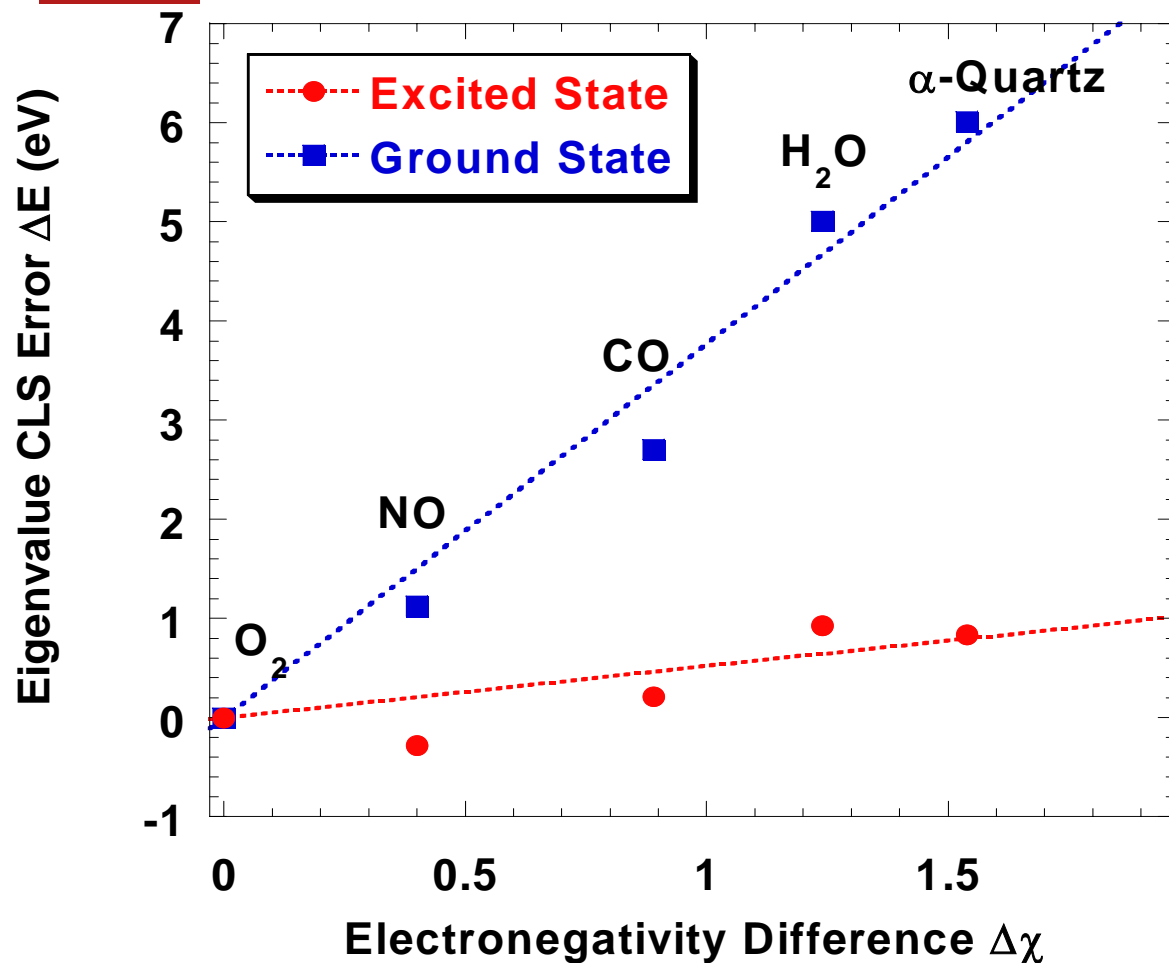


- Excited-state eigenvalue differences track the core-level shifts well

(0.6 eV rms error)

- Scatter in ground state is bad, but is there a trend?

Eigenvalue Errors vs Local Environment



- Errors tracks ionicity

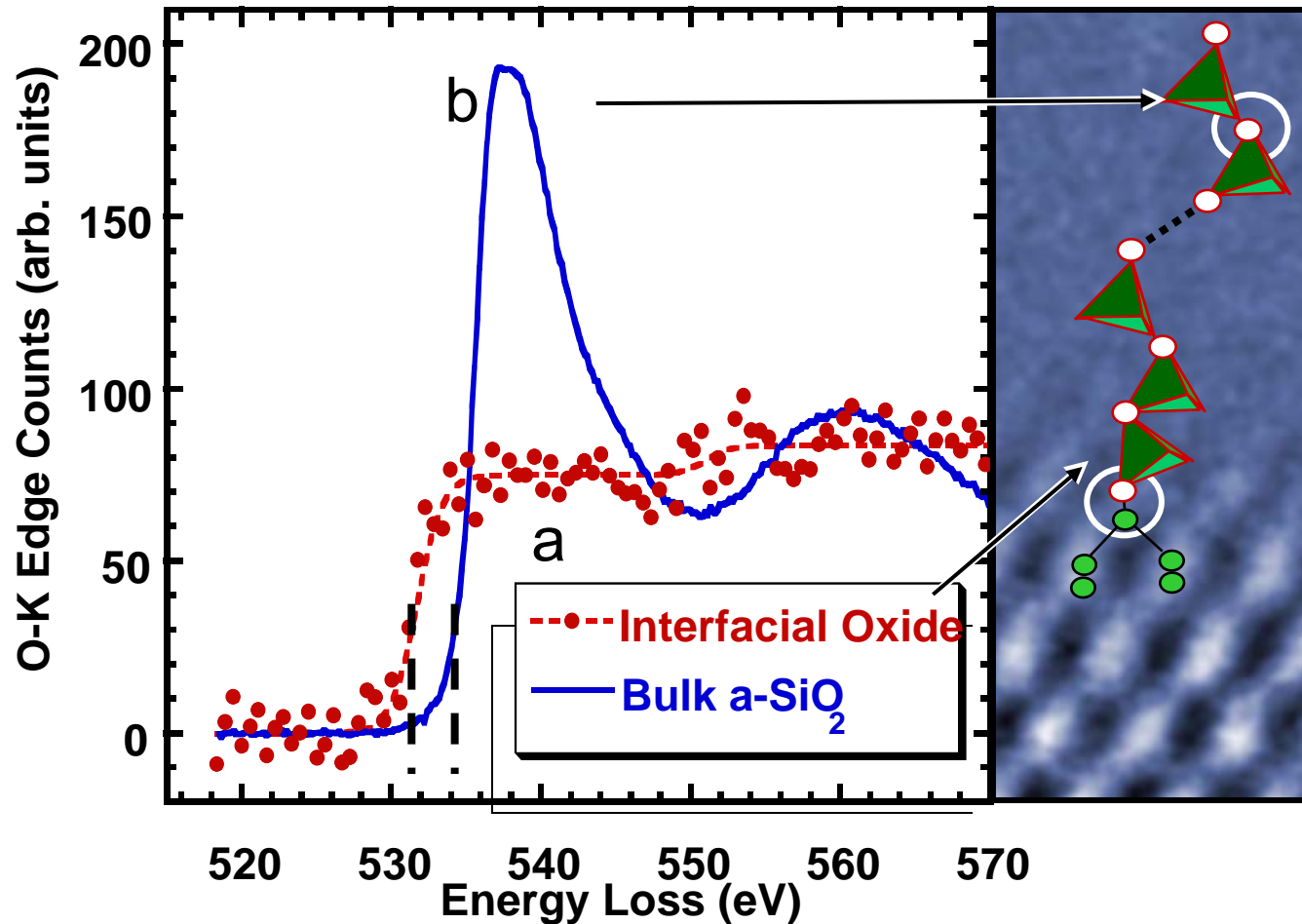
- Why?

Relaxation energy
depends on screening
from nearest neighbors.

Eigenvalues work well when comparing atoms in similar local environments

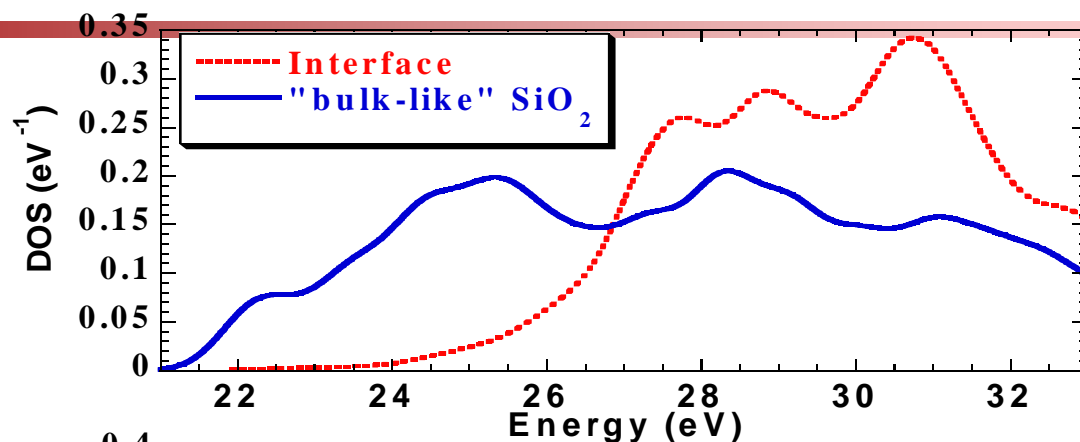


O K-edge of Si-SiO₂ Interface

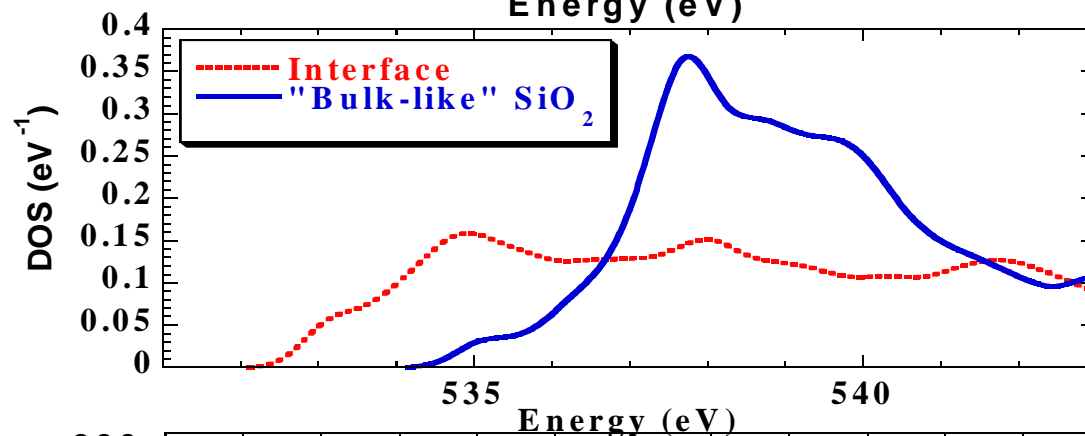


Band edge onset 3 eV lower at interface - fewer O neighbors

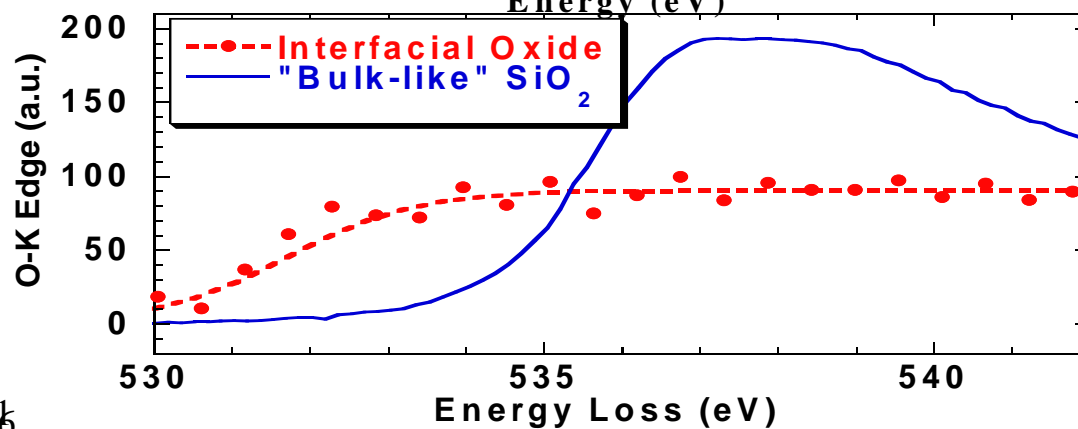
Oxygen K-edge at the Si/SiO₂ Interface



Ground-State
Theory



Excited-State
"Z+1 Approx"



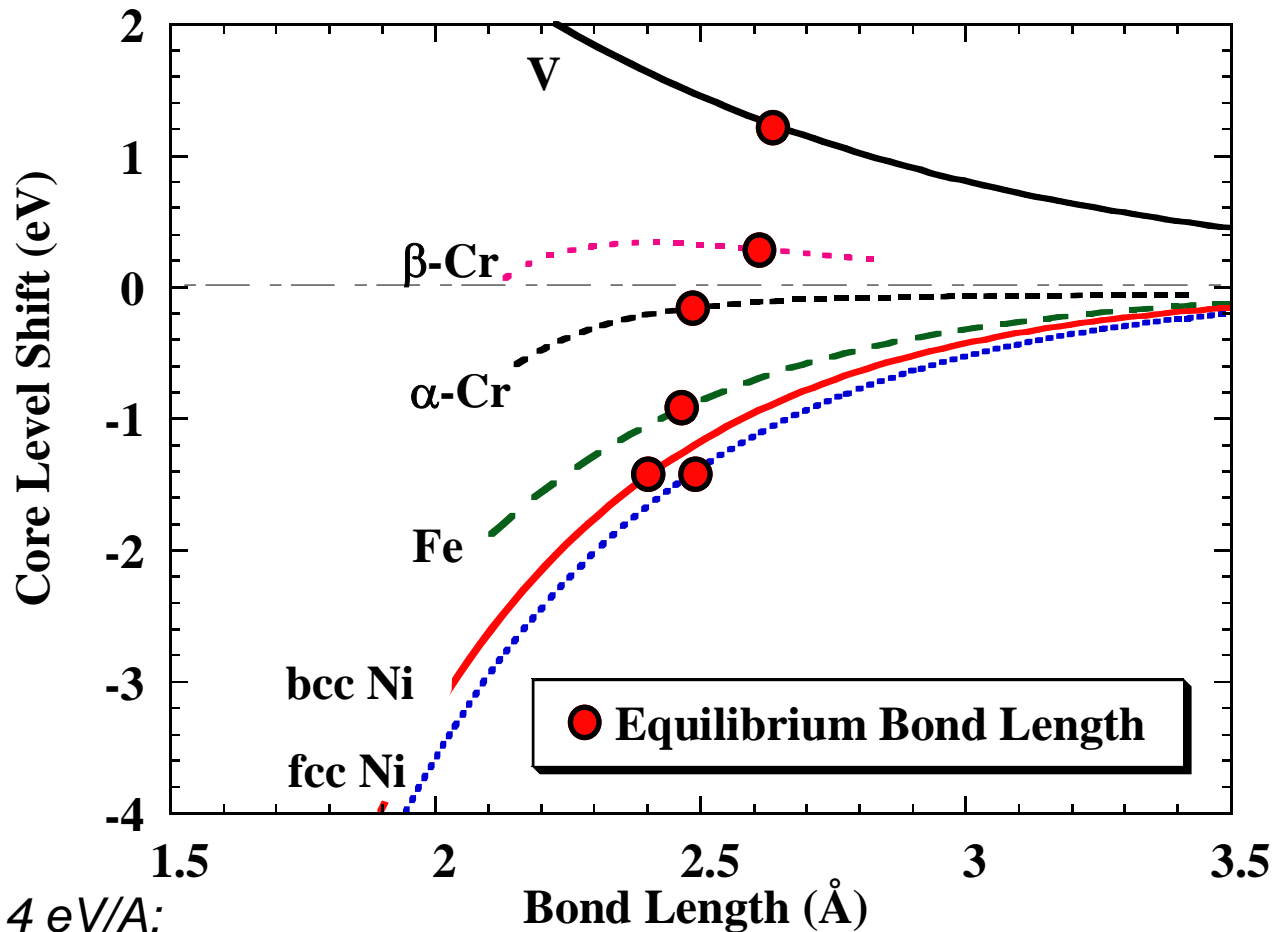
Experiment





EELS is very sensitive to Structural Changes

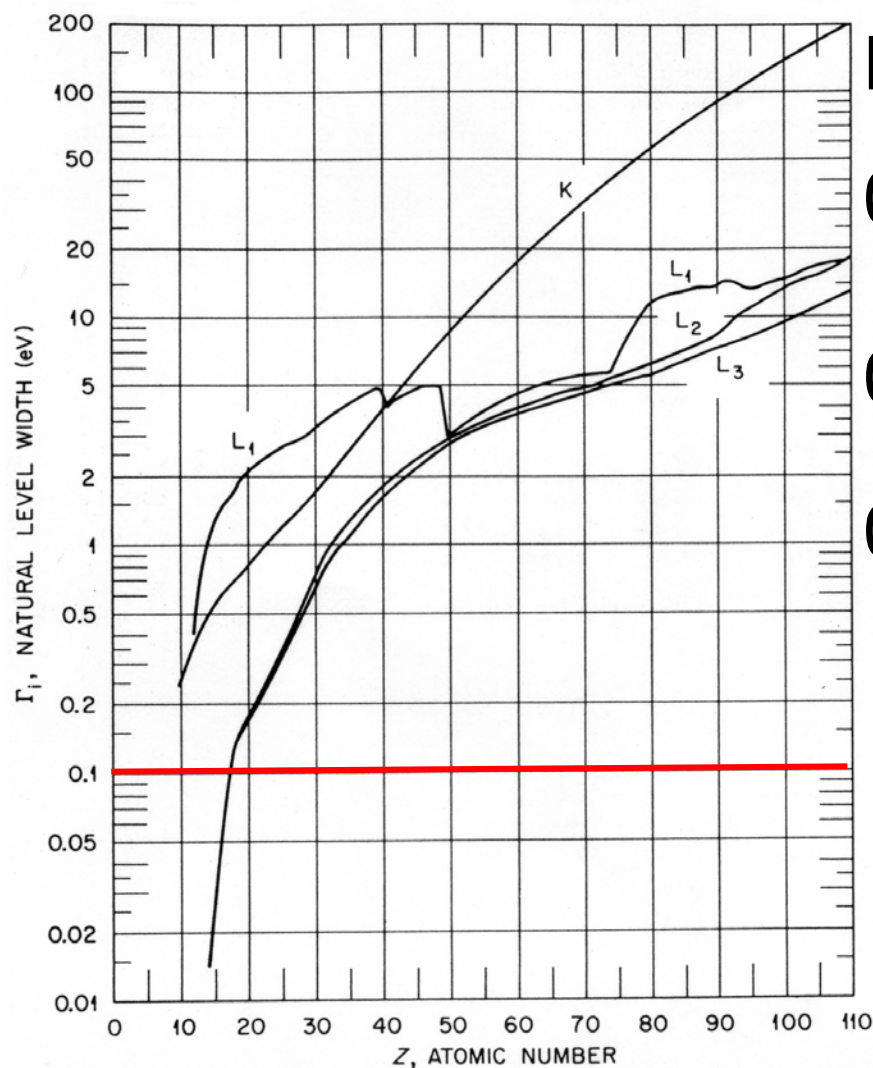
We expect $\text{CLS} \cong C (N_d - 5)/10 z^{1/2} \exp(-\kappa r)$



Moral: EELS calculations of defects must be done on relaxed structures



Core Hole Lifetimes



Resolution Limits:

0.1 eV $Z \sim 14$ (Si L_3 $\Gamma_i = 0.15$ eV)

0.2 eV $Z \sim 21$ (Sc L_3 $\Gamma_i = 0.19$ eV)

0.3 eV $Z \sim 25, 14$ (Na K $\Gamma_i = 0.30$ eV)

Better than 0.1 eV is still useful for valence EELS

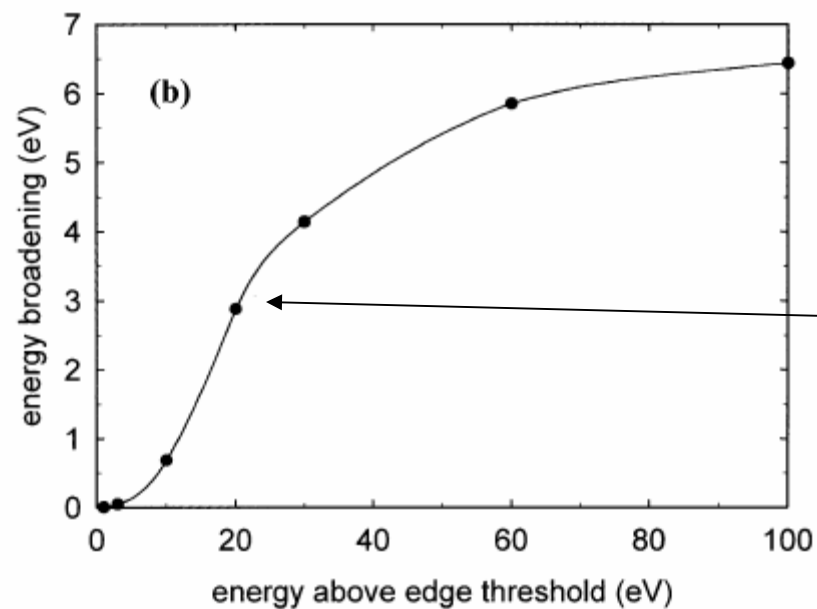
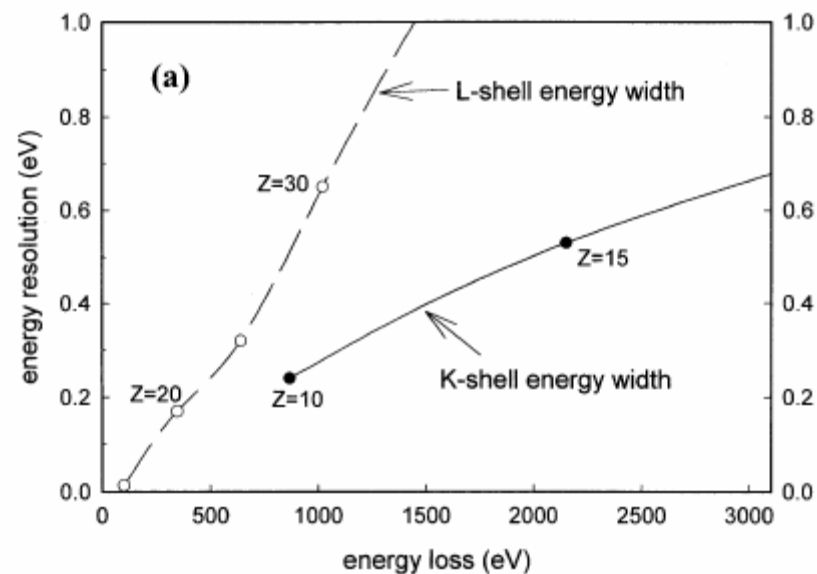
- image electrically active defects, -
- Doesn't require sub nm probe

Krause and Oliver, *J. Phys. Chem. Ref. Dat.* **8** (1979) 329.

David Muller 2006



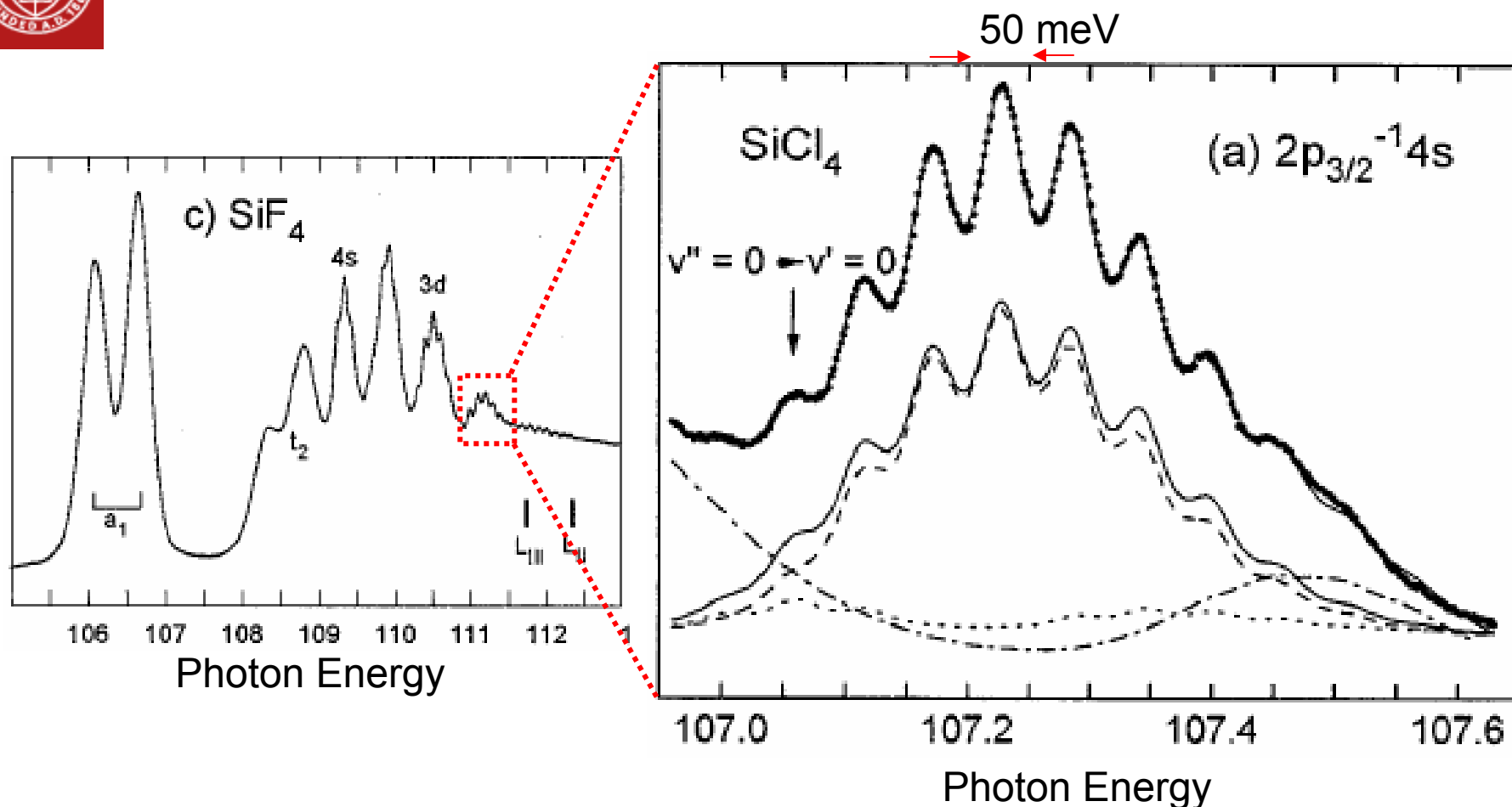
R.F. Egerton / *Micron* 34 (2003) 127–139



20 eV above the edge, no feature can be sharper than 3 eV

Fig. 6. (a) Natural width of K and L versus edge energy, based on data of [Krause and Oliver \(1979\)](#). (b) Final-state energy broadening as a function of energy above the ionization threshold, estimated using Eq. (1).

XAS of the Si $L_{2,3}$ Edge at 15 meV Energy Resolution

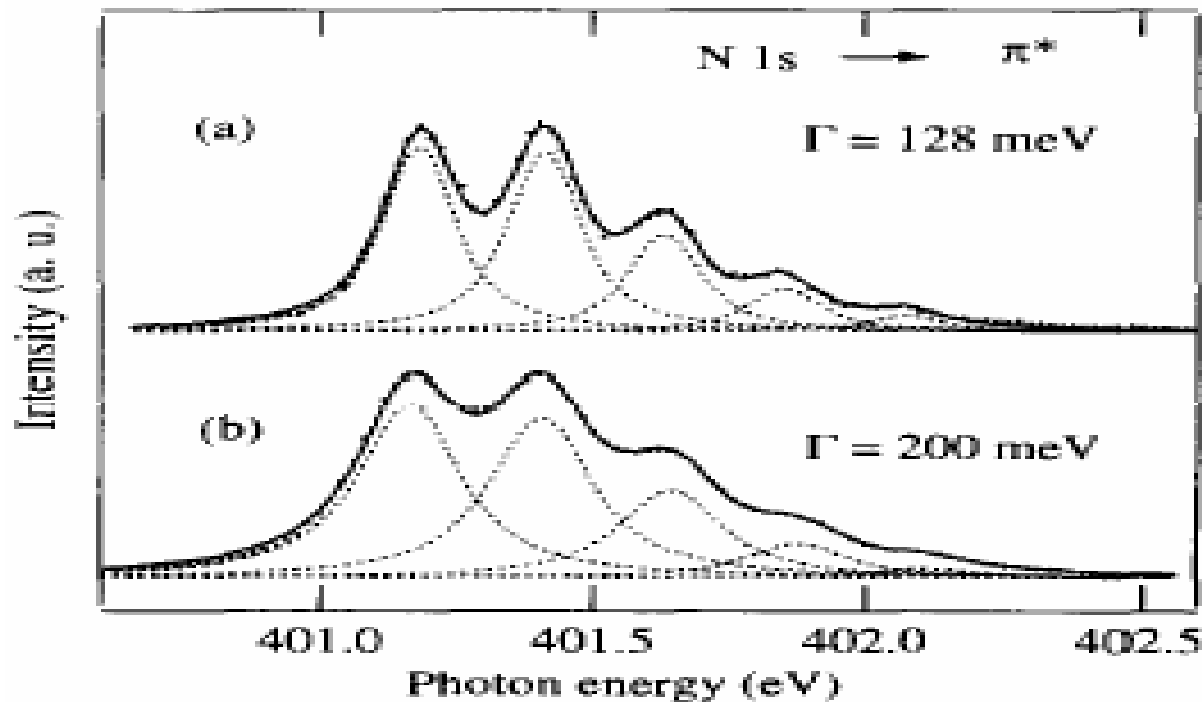


- Vibrational modes are important at 100 meV resolution
- Core hole lifetimes are measured at 50-80 meV (~ 50 – 100% larger than theory)

*R. Puttner et al, Phys. Rev. **A57** 297(1998).*



XAS of N-K in N_2



N_2 gas

N_2 in
Oxidized
TiAlN

Instrument resolution is 70 meV

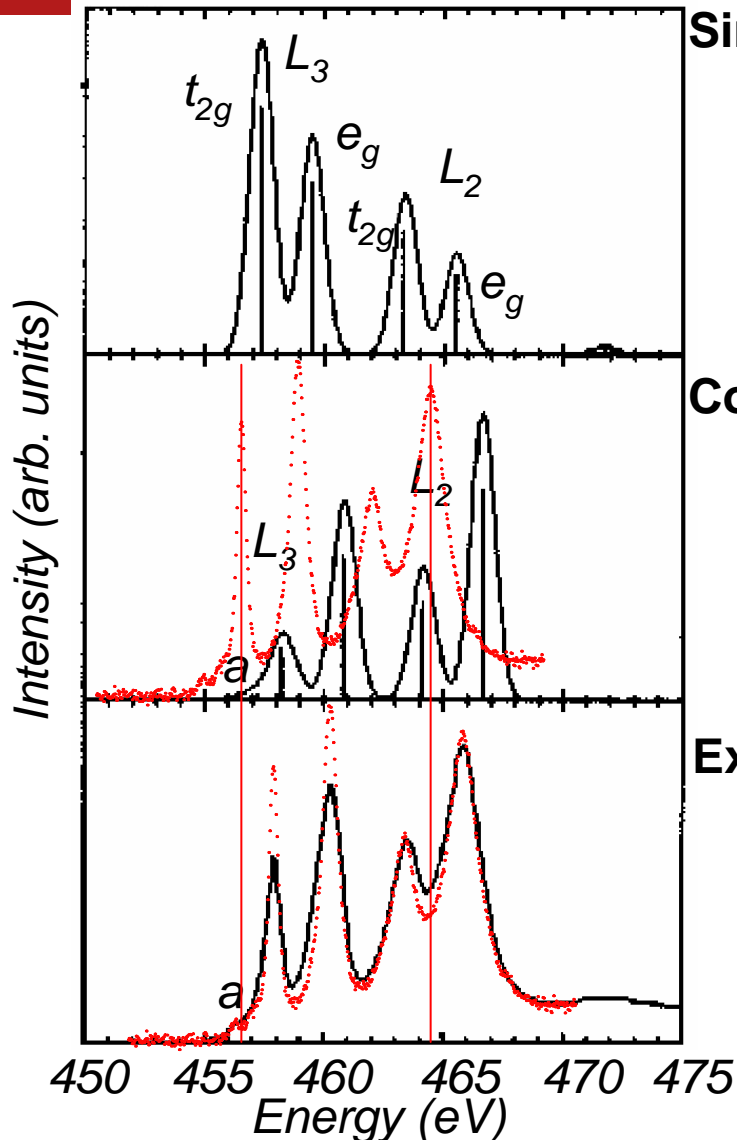
Vibrational states are resolved,

but **core-hole lifetime depends on the environment**

F. Esaka et al, J. Elec. Spectr. and Rel. Phen. 88-91 (1998) 817-820



Many-Body Corrections for the Ti-L Edge in SrTiO_3



Single Particle Theory: (Ogasawara, PRB 2001)

- includes core-hole self-consistently
- L_3 : $2p_{3/2} \rightarrow \text{Ti } 3d (t_{2g}, e_g)$
- L_2 : $2p_{1/2} \rightarrow \text{Ti } 3d (t_{2g}, e_g)$
- Wrong oscillator strengths and positions

Configuration-Interaction Theory: (Ogasawara 2001)

- 4 main peaks analogous to SP theory
- Peak a is multiplet of the $2p_{3/2} \rightarrow t_{2g}$
- No lifetime broadening (gaussian used)
- $2p$ spin-orbit splitting is too small

Experiment:

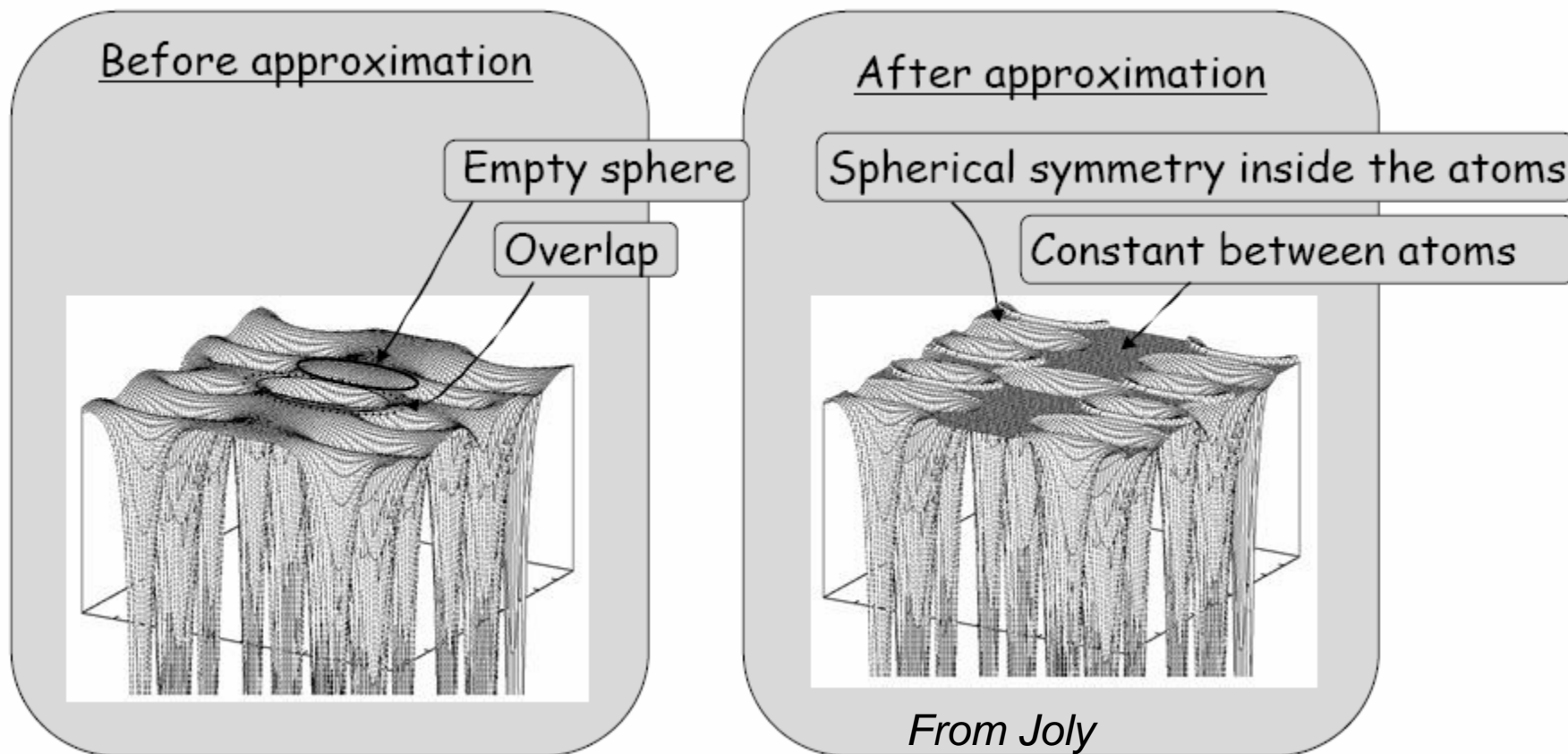
XAS: van der Laan 1990
(2 eV too high)

EELS: Muller 2002
100 meV resolution
50 meV absolute accuracy



The Muffin-Tin Approximation

This is a shortcut that makes it easier to solve Schrödinger's equation by approximating the potential



*A good approximation for close-packed structures like metals
(DOS inside spheres looks like an EELS final states)*



Calculation of the Final States

- *Cluster Methods: good for defects & clusters, often easier to run*
 - *Muffin-Tin Potential (OK for Metals, bad for semiconductors)*
 - *FEFF7 – no self-consistency: must guess charge transfers*
 - *FEFF8 – self –consistent: good for metals*
 - *Full Potential*
 - *FDMNES – no self-consistency, but it can input potentials from Wien2k*
- *Bandstructure methods: (3D periodic structures or supercells)*
 - *Almost all bandstructure codes are self-consistent now*
 - *Muffin-Tin Potential*
 - *LMTO – good for close-packed structures, esp. metals*
 - *Full Potential*
 - *FP-LAPW*
 - *Wien2k – easy to calculate matrix elements & core hole effects*
 - *Plane-wave codes (faster and less prone to artifacts than APW codes)*
 - *ABINIT (free, open-source and downloadable from abinit.org)*
 - *VASP (commercial)*
 - *CASTEP (commercial, fancy user interface)*



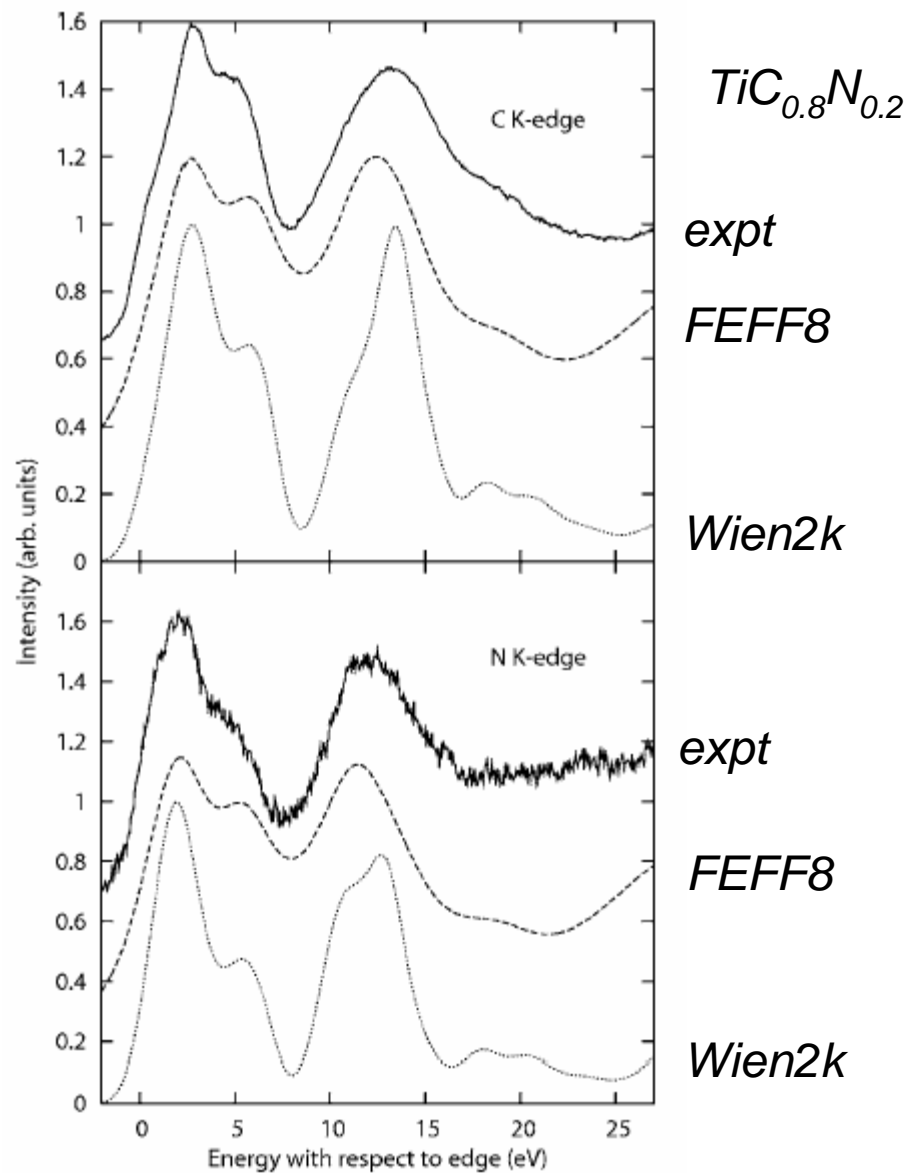
Many-Body Calculations

Strongly-correlated systems, and materials with large core-hole effects cannot be calculated using DFT codes. The options are limited

- *GW : Correct bandgap, but only a few atoms/supercell*
- *Configuration-Interaction (CI): very accurate for 1-6 atoms*
 - *good for transition metal oxide clusters*
- *Multiplet: (de Groot, van der Laan) single-atom in a crystal field*
 - *good for transition metal oxide crystals.*
 - *like CI, except it has adjustable parameters*



Wien2k vs FEFF8



Lionel Calmels, Claude Mirguet, and Yolande Kihn
PHYSICAL REVIEW B 73, 024207 (2006)